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STRUCTURE AND PROPERTIES OF POLYMERS AND ORGANOSILANES ADSORBED--ETC(U)  
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Structure and Properties of Polymers and Organosilanes  
Adsorbed Onto Oxidized Aluminum and Titanium,

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Interim Report for Period July 1, 1980 to June 30, 1981

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<p>The structure of films formed by organofunctional silanes adsorbed onto aluminum, titanium, and iron mirrors from aqueous solutions was related to the effectiveness of the silanes as primers for improving the wet strength of metal-to-metal adhesive joints made from the same metals. <math>\gamma</math>-aminopropyltriethoxysilane (<math>\gamma</math>-APS) formed smooth, continuous polysiloxane films when adsorbed</p>		

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onto iron from aqueous solutions at pH 8.0. Such films were extremely effective primers. Lap joints prepared from iron adherends primed with  $\gamma$ -APS at pH 8.0 retained about 70% of their original strength after 60 days immersion in water at 60°C while joints prepared from unprimed adherends retained only 25% of their strength.  $\gamma$ -APS was less effective when applied to iron adherends at pH 10.4 but lap joints prepared from such adherends still retained 50% of their strength after 60 days in water at 60°C.  $\gamma$ -glycidoxypyrroltrimethoxysilane ( $\gamma$ -GPS) formed polysiloxane films that were effective primers when adsorbed onto iron from aqueous solutions containing an acid to catalyze hydrolysis of the silane. The environmental failure of iron/epoxy lap joints was consistent with a model suggesting debonding of the adhesive a certain distance into the joint when a critical concentration of water was obtained that same distance into the joint.

When  $\gamma$ -APS was adsorbed onto aluminum from aqueous solutions at pH 8.5, low molecular polysiloxanes were obtained. When aluminum mirrors were immersed in aqueous solutions at pH 10.4 for more than a minute, the oxide was dissolved and low molecular weight siloxane polymers, possibly complexed with aluminum and copper, were formed on the surface.  $\gamma$ -APS and  $\gamma$ -GPS were both effective as primers for aluminum but were less effective than on iron.  $\gamma$ -GPS improved the wet strength of epoxy/aluminum joints by inhibiting corrosion of the substrate.

Films formed by adsorption of  $\gamma$ -APS from aqueous solutions onto titanium were composed of polysiloxanes similar to those obtained on iron and  $\gamma$ -APS was as effective a primer on titanium as on iron. Epoxy/titanium lap joints prepared from adherends pretreated with  $\gamma$ -APS at pH 8.0 or 10.4 were about twice as strong after 40 days in water at 60°C as joints prepared from unprimed adherends.

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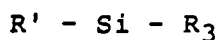
## I. Introduction

It is well known that strong adhesive bonds to the oxidized surfaces of metals may be obtained such that failure is almost invariably by cohesive fracture within the adhesive. However, moisture has an adverse effect on the strength of adhesive joints and after prolonged exposure to water even the most carefully prepared joints weaken and fail near the interface. As a result, there has been considerable interest in developing methods for improving the wet strength of adhesive bonds to metals. One way that this may be done is to produce an oxide on the surface of the metal that is particularly stable in the presence of water. This approach has, of course, been used for aluminum adherends and it has been found that the oxide obtained by anodizing aluminum in phosphoric acid is particularly stable and enables strong, durable adhesive bonds to be obtained to aluminum substrates.

An alternative is to utilize an organic material as a primer. It has been found that certain organofunctional silane compounds are extremely effective primers for improving the wet strength of metal to metal adhesive joints. For example, Kinloch (1) has considered  $\gamma$ -glycid-oxypropyltrimethoxysilane ( $\gamma$ -GPS) as a primer for improving the hydrothermal stability of aluminum tapered double cantilever beams bonded with an epoxy adhesive. When unprimed beams were statically loaded in water at 23°C, failure was always apparently interfacial but when the adherends were primed with a 1% aqueous solution of  $\gamma$ -GPS prior to bonding, the load required to produce failure in the same time was significantly increased and failure was cohesive within the epoxy resin. Patrick (2) used scanning electron microscopy to determine the locus of failure of tapered double cantilever beams prepared from 2024 aluminum alloy and bonded with an amine cured epoxy. When the samples were statically loaded in the presence of water, failure was initiated within the epoxy

resin but propagated along the adhesive/adherend interface. However, if the load was rapidly increased, the crack would again propagate within the resin. Thus, depending on the loading, failure could be made to alternate between interfacial and center-of-bond. However, when the aluminum adherends were primed with an aqueous solution of  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS) prior to adhesive bonding, interfacial failure was never obtained as long as the concentration of the  $\gamma$ -APS solution was about 0.01%. At higher or lower concentrations, interfacial failure was again obtained. Finally, it has been shown that  $\gamma$ -APS is also effective on titanium. Schrader and Cardamone (3) prepared lap joints by bonding titanium adherends with an epoxy adhesive. The joints were immersed in boiling water for 24 hours and then fractured in a tensile testing device while still wet. Joints prepared from adherends pretreated with a 1% solution of  $\gamma$ -APS before bonding always broke at a load about 1.5 times greater than joints prepared without such pretreatment.

Although several theories have been proposed to explain the mechanisms by which silanes function to improve the wet strength of adhesive joints (4), the "chemical bonding" theory is, perhaps, the most widely accepted (see Figure 1). Most useful silanes have the general structure



where R is a functional group that is easily hydrolyzed and R' is a functional group usually chosen for compatibility with a particular adhesive. According to the chemical bonding theory, the functional group R are hydrolyzed to form silanol (SiOH) groups when the silane is dissolved in water. When a metal adherend is subsequently immersed in the silane solution, the silane molecules are adsorbed onto the oxidized surface of the metal through the silanol groups. During subsequent drying, the silanols may condense with surface hydroxyl groups, forming

primary bonds with the oxide or may co-condense to form a siloxane polymer on the surface. The functional group R' may then react with an adhesive applied to the primed substrate.

The chemical bonding theory has provided a useful model for describing the mechanisms by which silanes function. However, little experimental evidence supporting the model has been reported. The objectives of this research are to determine the structure of films formed by the adsorption of  $\gamma$ -APS and  $\gamma$ -GPS onto the oxidized surfaces of aluminum and titanium primarily but also iron and to determine the effect that factors such as oxide structure and solution pH have on such adsorption. Finally, the relation between the structure of adsorbed silane films and their effectiveness as primers for improving the wet strength of metal to metal adhesive joints will also be determined.

Several analytical techniques, including X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), ellipsometry, and scanning electron microscopy (SEM) have been used for surface analysis in this research. However, a relatively new optical technique referred to as "reflection-absorption" infrared spectroscopy has been used rather extensively and is briefly described below.

## II. Reflection-Absorption Infrared Spectroscopy

Any attempt to obtain the infrared spectrum of a thin film on the surface of a metal necessarily involves a reflection experiment. The most important aspect of this experiment concerns the standing wave created by the combined incident and reflected beams. Under most circumstances this wave has nearly zero electric field amplitude at the surface of the metal and little interaction with a surface film is obtained. However, when large, almost grazing angles of incidence and radiation polarized parallel to the plane of incidence are used, the electric field amplitude of the standing wave at the surface of the metal is greatest and maximum interaction with a surface film is obtained.

The size or "depth" of an absorption band in reflection-absorption infrared spectroscopy may be obtained using the formalism given by Heavens (5). Consider a metal substrate with refractive index  $\tilde{n}_2 = n_2 - ik_2$  covered by a thin film with refractive index  $\tilde{n}_1 = n_1 - ik_1$  shown in Figure 2 and let the refractive index of the surrounding medium be  $n_0$ . When parallel polarized radiation is reflected from the filmed substrate as shown in Figure 2, the total electric field amplitude reflected back into the surrounding medium is given by

$$r = (r_1 + r_2 e^{-2i\delta_1}) / (1 + r_1 r_2 e^{-2i\delta_1}) \quad (1)$$

where

$$r_1 = \frac{n_0 \cos \phi_1 - \tilde{n}_1 \cos \phi_0}{n_0 \cos \phi_1 + \tilde{n}_1 \cos \phi_0} \quad (2)$$

$$r_2 = \frac{\tilde{n}_1 \cos \phi_2 - \tilde{n}_2 \cos \phi_1}{\tilde{n}_1 \cos \phi_2 + \tilde{n}_2 \cos \phi_1} \quad (3)$$

and

$$\delta_1 = (2\pi \tilde{n}_1 d_1 \cos \phi_1) / \lambda \quad (4)$$



The intensity of the reflected beam ("reflectivity") is given by  $R = rr^*$  where  $r^*$  is the complex conjugate of  $r$ . The "depth" of an absorption band is then obtained as

$$A = (R_0 - R)/R_0 \quad (5)$$

where  $R_0$  and  $R$  are the reflectivities for  $k_1 = 0$  and  $k_1 \neq 0$ .

When radiation polarized perpendicular to the plane of incidence is used, the analysis remains exactly the same but  $r_1$  and  $r_2$  are then obtained as (5)

$$r_1 = \frac{n_0 \cos \phi_0 - \tilde{n}_1 \cos \phi_1}{n_0 \cos \phi_0 + \tilde{n}_1 \cos \phi_1} \quad (6)$$

$$r_2 = \frac{\tilde{n}_1 \cos \phi_1 - \tilde{n}_2 \cos \phi_2}{\tilde{n}_1 \cos \phi_1 + \tilde{n}_2 \cos \phi_2} \quad (7)$$

These equations are rather difficult to solve by hand but are easily programmed for solution by computer techniques. The results obtained indicate that the band "depth"  $A$  for parallel polarized radiation is negligible for angles of incidence less than about  $50^\circ$  but then rises sharply, reaching a maximum near an angle of incidence of  $88^\circ$ . The band depth for perpendicular polarized light is always several orders of magnitude smaller.

The optimum angle of incidence of approximately  $88^\circ$  is difficult to obtain in practice. Most experiments are designed for an angle of incidence near  $80^\circ$ . Such angles are, of course, less than optimum and the band depths obtained from very thin films (e.g., monomolecular) are only marginally detectable using presently available infrared spectrophotometers. In order to obtain usable spectra from such thin films it is usually essential to enhance the band depth by making multiple reflections or by averaging several scans of the same spectral region. The number of reflections that can be used is related to the reflectiv-

ity of the substrate. The sensitivity of the infrared technique is, therefore, greatest for good reflectors such as copper, gold, silver, and aluminum and is somewhat less for moderate reflectors such as iron and titanium.

### III. Experimental

#### A. Infrared Spectroscopy

Iron sample mirrors for infrared spectroscopy were prepared by mechanically polishing "enameling iron" (Armco, Inc.). In the final step the mirrors were polished with 0.3 micron alumina polishing compound on billiard cloth. Aluminum sample mirrors were prepared by mechanically polishing 2024-T3 alloy (Alcoa) with magnesium oxide on kitten ear cloth. Titanium sample mirrors were prepared by mechanically polishing 6Al, 4V alloy (Colt Industries, Inc.) using alumina polishing compound on billiard cloth.

After polishing was completed the mirrors were rinsed repeatedly in distilled water and then blown dry with nitrogen. Such mirrors were hydrophilic but became hydrophobic during exposure to the laboratory atmosphere. As a result, only freshly polished mirrors were used as substrates for infrared spectroscopy.

Films were formed by the adsorption of silanes from aqueous solutions onto the mirrors as described below. The mirrors were then mounted in a reflection accessory (Harrick Scientific Co.) in the sample beam of the infrared spectrophotometer (Perkin-Elmer Model 180). Polished but unfilmed mirrors were mounted in a second reflection accessory in the reference beam, enabling all infrared spectra to be recorded differentially. A AgBr wire grid polarizer was used to isolate the parallel polarized component of the infrared radiation entering the monochromator. The spectrophotometer was continuously purged with dried air to eliminate absorption bands due to atmospheric moisture.

The reflection accessories were actually configured in two different ways depending on the reflectivity of the metal substrates. For titanium (moderately reflecting in the infrared region) the configura-

tion shown in Figure 3A, providing a single reflection at any angle of incidence, was used. For iron and aluminum (good reflectors), the configuration shown in Figure 3B, providing any number of reflections at a fixed angle of incidence ( $78^\circ$ ) was used.

#### B. Ellipsometry

In some cases the sample mirrors were examined immediately before and after adsorption of the silanes using an ellipsometer (Rudolph Research Model 436). This procedure enabled the thicknesses of the oxides and the adsorbed films to be determined.

#### C. X-Ray Photoelectron and Auger Electron Spectroscopy

Samples for X-ray photoelectron and Auger electron spectroscopy were prepared in the same way as samples for infrared spectroscopy and were then stored in a dessicator until they were ready for use (usually the following day). XPS and AES spectra were mostly obtained using Physical Electronics spectrometers at Bell Laboratories in Columbus, Ohio. However, a few AES spectra were obtained using a Physical Electronics spectrometer at Armco, Inc. in Middletown, Ohio.

#### D. Adhesive Joints

Single lap shear adhesive joints were prepared according to ASTM Standard D1002. Pairs of metal adherends ( $4.0 \times 1.0 \times 0.063$  in.) were polished as described above. In some cases the adherends were then immersed in aqueous solutions of silane at the appropriate pH and concentration for thirty minutes and then blown dry in a stream of nitrogen. In other cases the adherends were left untreated as a control. In all cases, pairs of similarly prepared adherends were bonded together using an adhesive consisting of an epoxy resin (Epon 828, Shell Chemical Co.) and 9.4 weight percent of a tertiary amine curing agent (Ancamine K-61B, Pacific Anchor Chemical Co.). The adhesive was cured for four days at room temperature and one hour at  $100^\circ\text{C}$ . The joints were then cooled to

room temperature and immersed in a water bath at 60°C. At appropriate intervals joints were removed from the bath and drawn in an Instron Universal Testing Instrument at a rate of 0.05 in/min and the force required to break the joints was determined.

#### IV. Results and Discussion

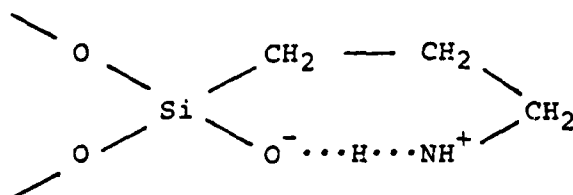
##### A. Iron substrates

Freshly polished iron mirrors were characterized using Auger electron spectroscopy and ellipsometry. Results obtained from ellipsometry indicated that such mirrors were typically covered by an oxide 25-50 Å thick. Results obtained from AES indicated that the only elements present on the surfaces of the mirrors were carbon, oxygen, iron, and zinc (see Figure 4A). Most of the carbon was undoubtedly due to adsorbed hydrocarbons while the zinc was probably present in the water used in the polishing operation. The iron and oxygen were, of course, related to the oxide. When the surface was sputtered for ten minutes, the zinc signal disappeared completely and the carbon and oxygen signals were greatly reduced in intensity (see Figure 4B). At the same time the iron signal increased considerably. These results confirmed that the oxide was only a few tens of angstroms in thickness.

The infrared spectra of films formed by  $\gamma$ -APS adsorbed onto iron mirrors from 1.0% aqueous solutions at pH 10.4 and pH 8.0 are shown in Figures 5A and B, respectively. Spectra of films formed at pH = 10.4 are characterized by strong absorption bands near 1550, 1470, and 1130  $\text{cm}^{-1}$  and by weaker bands near 1320 and 2920  $\text{cm}^{-1}$ . The transmission infrared spectrum of  $\gamma$ -APS is characterized by strong infrared absorption bands near 960, 1080, 1105, 2855, 2880, 2920, and 2970  $\text{cm}^{-1}$  that are characteristic of  $\text{SiOCH}_2\text{CH}_3$  groups (6). The absence of these bands from the spectrum shown in Figure 5A indicates that  $\gamma$ -APS is in fact hydrolyzed in an aqueous solution to form silanol ( $\text{SiOH}$ ) species. The strong band near 1130  $\text{cm}^{-1}$  in Figure 5A is assigned to an  $\text{SiOSi}$  vibration, indicating that the silanol species have condensed on the oxidized iron surface to form siloxane polymers.

The bands near 1550 and 1470  $\text{cm}^{-1}$  in  $\gamma$ -APS films formed at pH 10.4

(see Figure 5A) have been the subject of considerable discussion. Neither of these bands is observed in transmission spectra of  $\gamma$ -APS (6) and it has been thought that these bands might be related to an internal zwitterion (7)



or to interaction of the silane with the oxide through the amino group (8). However, we have recently determined that bands can be observed near these frequencies in transmission infrared spectra of certain fatty amines. For example, bands are observed near  $1565$  and  $1485\text{ cm}^{-1}$  in infrared spectra of lauryl amine (9). It is known that primary amines can absorb carbon dioxide to form bicarbonate species (10) and it may be that the bands near  $1565$  and  $1485\text{ cm}^{-1}$  for lauryl amine are related to such species. This assignment was confirmed by an experiment to remove absorbed carbon dioxide from the lauryl amine (9). A small amount of the amine was deposited onto a KBr disc. The infrared spectrum obtained from this sample was characterized by the abovementioned bands near  $1565$  and  $1485\text{ cm}^{-1}$ . The KBr disc was then warmed in air for about an hour and then transferred to the infrared spectrophotometer which was purged with nitrogen. The spectrum obtained in that case was characterized by bands near  $1610$  and  $1460\text{ cm}^{-1}$  that can be assigned to the deformation modes of free amino and methylene groups, respectively. When the KBr disc was maintained in the nitrogen atmosphere, the bands near  $1485$  and  $1565\text{ cm}^{-1}$  did not appear. However, these bands did reappear when the disc was exposed to the laboratory atmosphere for about half an hour.

In a separate experiment, reflection-absorption infrared spectroscopy was used to determine the structure of  $\gamma$ -APS films adsorbed onto

iron mirrors from aqueous solutions under conditions that were free of carbon dioxide (9). Samples were prepared in a nitrogen-purged glovebox located above the sample chamber of the infrared spectrophotometer. Immediately after preparation, the samples were lowered through the bottom of the glovebox and mounted in the reflection accessory in the sample beam of the spectrophotometer (which was also purged with nitrogen). The infrared spectrum obtained from one such pair of mirrors is shown in Figure 6A. Strong bands are observed near 1040 and 1130  $\text{cm}^{-1}$  as are weaker bands near 2850 and 2420  $\text{cm}^{-1}$ . However, only weak absorption was obtained between 1400 and 1700  $\text{cm}^{-1}$ . The sample mirrors were then maintained in the spectrophotometer but the purge gas was switched to dried air. After a few hours, the spectrum shown in Figure 6B was obtained. Absorption bands near 1470 and 1570  $\text{cm}^{-1}$  were again observed. Although the formation of a zwitterion structure can not be ruled out, the results described above indicate that the bands observed near 1470 and 1570  $\text{cm}^{-1}$  in infrared spectra of  $\gamma$ -APS films formed on iron at pH 10.4 are probably related to a bicarbonate species.

Infrared spectra of  $\gamma$ -APS films formed on iron at pH 8.0 (see Figure 5B) are characterized by a strong absorption band near 1135  $\text{cm}^{-1}$  and by much weaker bands near 1500 and 1600  $\text{cm}^{-1}$ . Again, the band near 1135  $\text{cm}^{-1}$  is assigned to an SiOSi vibration, indicating polymerization of  $\gamma$ -APS on the oxidized iron surface. The bands near 1500 and 1600  $\text{cm}^{-1}$  are assigned to vibrational modes of  $\text{NH}_3^+$  groups, indicating formation of hydrochlorides (HCl was used to acidify the  $\gamma$ -APS solutions).

Results obtained from X-ray photoelectron spectroscopy were in good agreement with those obtained from infrared spectroscopy (9). Portions of the XPS spectra obtained from  $\gamma$ -APS films formed at pH 8.0 and 10.4 are shown in Figures 7 and 8, respectively. For films formed at pH = 8.0, the nitrogen 1s binding energy was split into two components near 399.6



and 401.5 eV that may be assigned to free ( $\text{NH}_2$ ) and protonated ( $\text{NH}_3^+$ ) amino groups, respectively. For films formed at pH 10.4, the nitrogen 1s binding energy had only a single component near 399.6 eV, indicating that the bicarbonate species was unstable in the vacuum system of the XPS spectrometer. The XPS results did not depend significantly on film thickness. Similar results were obtained from films about 100 Å thick that were adsorbed from 1% solutions and from films about 20 Å thick that were adsorbed from 0.4% solutions (see Figures 7 and 8).

The oxygen 1s binding energy was always composed of components near 532.0 and 530.5 eV that were characteristic of the polysiloxane and the oxide, respectively. For the 100 Å films the component near 532.0 eV was always stronger but for the 20 Å films the component near 530.5 eV was stronger. Such results are, of course, expected for continuous films of varying thickness. The continuous nature of the films was verified using Auger electron spectroscopy to obtain silicon Auger images from similarly prepared films. No evidence for formation of primary bonds between  $\gamma$ -APS and the oxidized surface of iron mirrors was obtained from XPS.

Somewhat similar results have been obtained for  $\gamma$ -GPS. The transmission infrared spectrum of  $\gamma$ -GPS is shown in Figure 9A. The spectrum is characterized by strong absorption bands near 1200, 1085, and 820  $\text{cm}^{-1}$ . Weak bands are observed near 1465, 1410, 1385, 1335, 1264, 912, 855, and 780  $\text{cm}^{-1}$ . The band near 1200  $\text{cm}^{-1}$  is assigned to a methyl rocking mode of the  $\text{SiOCH}_3$  groups and the bands near 1085 and 820  $\text{cm}^{-1}$  are assigned to SiOC stretching modes of the same group. The weaker bands near 1264, 912, and 855  $\text{cm}^{-1}$  are assigned to stretching modes of the epoxy ring. The remaining weak bands are undoubtedly due to  $\text{CH}_2$  deformation modes in the glycidoxypropyl functional groups.

The structure of films formed by the adsorption of  $\gamma$ -GPS onto iron

mirrors from aqueous solutions has also been investigated using infrared spectroscopy. However,  $\gamma$ -GPS was found to be a rather poor film former and although several different deposition techniques were investigated, only discontinuous films with poorly reproducible thicknesses were usually obtained. The best films were obtained by adding a few drops of acetic acid to 1% aqueous solutions of  $\gamma$ -GPS to catalyze hydrolysis of the silane and then hydrolyzing the silane for an appropriate time before immersing the iron mirrors. The mirrors were then withdrawn at a constant rate (usually 0.125 in/min) using a motorized device constructed for this purpose. The spectrum shown in Figure 9B was obtained from iron mirrors that were immersed for 60 minutes in a solution that had been pre-hydrolyzed for 30 minutes. In this case the bands near 820 and 1200  $\text{cm}^{-1}$  are considerably reduced in intensity, indicating substantial hydrolysis of the silane. However, a strong band is observed near 1120  $\text{cm}^{-1}$ , indicating polymerization to form a polysiloxane on the surface.

The thickness of the  $\gamma$ -GPS films was closely related to the concentration of the solutions. Films about 100 Å thick were formed from 1% aqueous solutions. Nearly monomolecular films were formed from more dilute solutions but the spectra of such films were similar to spectra of thicker films. No evidence for the formation of primary bonds between the silane and the oxide was obtained from infrared spectroscopy or XPS.

These results indicate that the chemical bonding theory can be at least partially supported. There is no doubt that the silanes are hydrolyzed in aqueous solutions and that the silanes polymerize during drying to form polysiloxanes. However, no evidence for formation of primary bonds between the oxide and the silanes was obtained using XPS or infrared spectroscopy. Accordingly, it must be concluded that interaction between  $\gamma$ -APS and  $\gamma$ -GPS and the oxidized iron surface most likely

involves hydrogen bonding.

As indicated above, we have prepared single lap shear adhesive joints in order to determine the effectiveness of  $\gamma$ -APS and  $\gamma$ -GPS as primers for improving the wet strength of iron/epoxy adhesive joints and to determine the relation between silane structure and such effectiveness (9). The results are shown in Figure 10. Joints prepared from adherends pretreated with silane solutions prior to adhesive bonding were always much stronger than joints prepared from unprimed adherends. The greatest improvement in wet strength for joints primed with  $\gamma$ -APS was obtained when the primer was applied from solutions acidified by addition of HCl. Unprimed joints retained only about 25% of their strength after 60 days immersion at 60°C. Joints prepared with  $\gamma$ -APS primer at pH 10.4 retained about 50% of their strength after 60 days but joints prepared with  $\gamma$ -APS primer at pH 8.0 retained about 70% of their strength after such immersion. Joints primed with 1% aqueous solutions of  $\gamma$ -GPS acidified by addition of a few drops of acetic acid retained about 55% of their original strength after 60 days.

The results shown in Figure 10 could be interpreted in several ways. The stress distribution in single lap joints has been considered by several groups (11,12) and has been shown to be very non-uniform. The maximum shear stress in the adhesive in such joints is at the ends of the lap and can be several times greater than the average shear stress (11,12). DeVries calculated the maximum shear stress in dry aluminum/epoxy lap joints and showed that failure in such joints occurred when a particular maximum shear stress was obtained (11). However, a failure criterion based only on the maximum shear stress in a lap joint cannot be used to interpret the results for water soaked joints shown in Figure 10.

A very simple alternative was suggested by a model for the environmental degradation of iron/epoxy butt joints that was recently proposed

by Kinloch (13). It was suggested that the loss in strength of an adhesive joint exposed to water can be explained in terms of diffusion of water into the joint and the accumulation of a critical concentration of water a certain distance into the joint, causing "debonding" over that same distance. For the case of lap joints used in our work, this would mean that the edges of the joint would "debond" during water immersion and that the size of the "bonded" area near the center of the joint would gradually decrease as the critical concentration was obtained further and further into the joint due to continuing water diffusion into the joint.

The average shear stress in the joint is given by  $\tau = F/A$  where  $F$  is the force applied to the adherends and  $A$  is the bonded area. If it is assumed that the joint fails when a critical average shear stress ( $\tau_c$ ) is obtained in the joint, then the force required to produce failure should be given by  $F_c = \tau_c A$ . The bonded area ( $A$ ) can be determined by solving the equation for diffusion of water into a rectangular joint and the breaking strength ( $F_c$ ) of the joint can be measured experimentally. A plot of  $F_c$  versus  $A$  should be a straight line passing through the origin and having a slope equal to  $\tau_c$ .

The equation for diffusion of water into a rectangular area  $\{-a \leq x \leq a, -b \leq y \leq b\}$  is (14)

$$\frac{\partial C}{\partial t} = D \left\{ \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right\} \quad (8)$$

where  $C$  is the concentration at the point  $(x, y)$  inside the rectangular area at time  $t$  and  $D$  is the diffusion coefficient. The solution to this equation is given as (15)

$$C(x, y) = C(\infty) [1 - \phi(a, x) - \phi(b, y)] \quad (9)$$

where  $C(\infty)$  is the maximum water absorption by the adhesive,

$$\phi(a, x) = \frac{4}{\pi} \sum_{n=0}^{\infty} \left[ \frac{(-1)^n}{(2n+1)} \right] \exp \left[ -(2n+1)^2 \pi^2 D t / 4a^2 \right] \cos \left[ (2n+1) \pi x / 2a \right], \quad (10)$$

$\phi(b,y)$  has a similar form. Using equation 9, the concentration of water at any point in a lap joint can be calculated as a function of time. Moreover, for any particular time, a contour connecting all points having a given concentration can be drawn.

Kinloch has measured the maximum water absorption and the diffusion coefficient for water in the adhesive used here as 2.20 gms per 100 gms of adhesive and  $18.1 \times 10^{-9} \text{ cm}^2/\text{sec}$  at  $60^\circ\text{C}$  and has suggested that the critical concentration for "debonding" the adhesive from an iron substrate is about 1.37 gms of water per 100 gms of adhesive (13). A computer program was written to solve equation 9 and contours showing the critical concentration of water in a lap joint as a function of time were constructed. The results for 10, 40, and 60 days are shown in Figure 11. The "bonded" area (A) is the area inside the contours where the concentration is below the critical concentration and is shaded for the case of sixty days immersion.

As indicated above, plots of breaking strength ( $F_c$ ) versus "bonded" area (A) should be straight lines passing through the origin and having a slope equal to the critical shear strength ( $T_c$ ). Plots of  $F_c$  versus A for unprimed joints and joints primed with  $\gamma$ -GPS are shown in Figure 12. The data obviously fit the model quite well. The data for joints primed with  $\gamma$ -APS did not fit the model unless the critical concentration was assumed to increase to about 1.56 gms of water per 100 gms of adhesive. The results obtained in that case are also shown in Figure 12. Once again good agreement with the model is obtained.

Reference to Figure 12 indicates that for this model, the critical concentration of water is the same for unprimed joints and joints primed with  $\gamma$ -GPS. However, the critical shear strength is much higher for joints primed with  $\gamma$ -GPS. This seems to indicate that the  $\gamma$ -GPS primer results in an interface that is just as susceptible to water as that of

the unprimed joints but has greater mechanical strength. Reference to Figure 12 also indicates that the  $\gamma$ -APS primer results in an interface that is less susceptible to water (i.e., a greater critical concentration of water is required for "debonding") and has greater mechanical strength than the interface of the unprimed joints.

Another interpretation of the results shown in Figure 10 was suggested by a model recently proposed by Andrews for the hydrothermal degradation of epoxy/titanium adhesive joints (16). According to Andrews, the epoxy/titanium interface consists of strong, primary bonds having bond energy  $U_A$  and weaker bonds having energy  $U_B$  that are obtained by hydrolysis of the primary bonds. The intrinsic interfacial fracture energy is then obtained as

$$\theta_0(t) = n(t)U_A + (N-n(t))U_B = n(t)(U_A-U_B) + NU_B \quad (11)$$

where  $N$  is the total number of interfacial bonds and  $n(t)$  is the number of primary interfacial bonds. Assuming that the hydrolysis reaction follows first order kinetics,

$$n(t) = Ne^{-kt} \quad (12)$$

where  $k$  is a rate constant. Then,

$$\theta_0(t) = (U_A-U_B)Ne^{-kt} + NU_B \quad (13)$$

Now,  $\theta_0(0)$  obviously equals  $NU_A$  and  $\theta_0(\infty)$  equals  $NU_B$ . The intrinsic interfacial fracture energy is then obtained as

$$\theta_0(t) = \{\theta_0(0) - \theta_0(\infty)\}e^{-kt} + \theta_0(\infty) \quad (14)$$

The two models described above give the breaking strength and fracture energy as a function of time in an aggressive environment and can not be compared rigorously. However, it is felt that breaking strength and fracture energy have similar dependence on time and that the two models can be compared qualitatively. It may then be observed that both

models predict that breaking force decreases exponentially with time. The essential difference between the two models is that the former predicts that the breaking strength of a joint will drop to zero when the critical concentration of water is obtained at all points in the joint while the latter predicts a residual, finite breaking strength. Reference to Figures 10 and 12 indicates that for iron/epoxy lap joints the breaking strength generally does decrease exponentially with increasing immersion time and reference to Figure 12 indicates that breaking strength does extrapolate to zero for small values of A (i.e., long immersion times). However, fracture energies and breaking strengths at longer times may have to be determined in order to determine which model best represents the environmental degradation of iron/epoxy lap joints.

#### B. Aluminum substrates

There has been considerable discussion regarding the nature of the oxides formed on aluminum adherends during various hydrothermal, etching, and anodization treatments. Therefore, the first phase of this research was concerned with determining the structure of the oxides on 2024 aluminum mirrors. When freshly polished mirrors were characterized using AES (see Figure 13), the only elements detected in significant quantities were aluminum and oxygen, indicating that the air-formed oxide was probably an amorphous  $\text{Al}_2\text{O}_3$ . Small amounts of carbon and copper were also detected. Copper is, of course, the major alloying element in 2024. The carbon was rapidly removed during sputtering and was undoubtedly due to adsorbed hydrocarbons.

Infrared spectra of freshly polished mirrors were characterized by an intense absorption band near  $960\text{ cm}^{-1}$  (see Figure 14A) that was assigned to an AlO stretching vibration in amorphous  $\text{Al}_2\text{O}_3$ . When mirrors were immersed in boiling distilled water for five minutes, spectra similar to that in Figure 14B were obtained. These spectra were character-

ized by absorption bands near 3399, 3099, 1640, 1375, 1080, 847, and  $650\text{ cm}^{-1}$  and the oxide was readily identified as pseudoboehmite ( $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}, \text{X} \approx 2$ ).

When the temperature of the water treatment was lowered, the rate at which the natural oxide transformed to pseudoboehmite was also reduced. Only the natural oxide was observed after five minutes at  $63^\circ\text{C}$  but only pseudoboehmite was observed after sixty minutes. The conversion of the natural oxide to pseudoboehmite at  $40^\circ\text{C}$  is shown in Figure 15. Only the natural oxide was observed after one hour (Figure 15A) but pseudoboehmite began to appear after sixteen hours (Figure 15B) and only pseudoboehmite was observed after 24 hours (Figure 15C). At room temperature the natural oxide was the only oxide present after 22 hours.

These results differ somewhat from those previously reported (17) relating the strength of epoxy/aluminum adhesive joints to the hydrothermal treatment given to the adherends prior to adhesive bonding. The strength of joints prepared from adherends immersed in distilled water at  $10^\circ\text{C}$  reached a maximum after about 30 minutes immersion time and then slowly decreased as immersion time was increased. It was suggested that this behavior was related to the formation after 30 minutes of a thin layer of bayerite ( $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) that strongly adsorbed the epoxy adhesive. It was also suggested that increased immersion time resulted in thicker films of bayerite that were mechanically weak, resulting in the decreased joint strengths observed for long immersion times. However, the results obtained here indicate that bayerite is not formed by a simple hydrothermal treatment of mechanically polished 2024 alloy. What is observed is the transformation of amorphous  $\text{Al}_2\text{O}_3$  to pseudoboehmite at a rate that increases with temperature.

Films of  $\gamma$ -APS were formed on freshly polished aluminum mirrors by immersing the mirrors in 1% aqueous solutions of  $\gamma$ -APS for appropriate



times, withdrawing the mirrors, and blowing the excess solution off the mirrors using a strong stream of nitrogen. The structure of such films was then determined as a function of pH and immersion time using infrared spectroscopy. The results are shown in Figure 16. Films formed by adsorption from solutions acidified to pH 8.5 by addition of HCl were characterized by absorption bands near 3300, 3000, 1600, 1500, and 1080  $\text{cm}^{-1}$ . The bands near 1600 and 1500  $\text{cm}^{-1}$  may be assigned to deformation vibrations of protonated amino ( $\text{NH}_3^+$ ) groups while the broad band near 3000  $\text{cm}^{-1}$  may be assigned to the stretching modes of the same groups, indicating that  $\gamma$ -APS is probably adsorbed as a hydrochloride at pH 8.5. The band near 3300  $\text{cm}^{-1}$  is undoubtedly due to the stretching vibrations of silanol ( $\text{SiOH}$ ) groups, indicating that the adsorbed  $\gamma$ -APS is highly hydrolyzed. The strong band near 1080  $\text{cm}^{-1}$  is undoubtedly due to an  $\text{SiO}$  asymmetric stretching mode, indicating that some of the silanols condensed on the surface to form siloxane polymers. It is interesting to note that the corresponding band for  $\gamma$ -APS adsorbed onto iron at comparable pH values (Figure 5B) is near 1130  $\text{cm}^{-1}$ . It is felt that the low frequency observed for the  $\text{SiO}$  stretching mode indicates that  $\gamma$ -APS is adsorbed onto aluminum as low molecular weight oligomers, possibly because of a strong interaction between  $\gamma$ -APS and the oxidized surface of aluminum.

When films were formed by the adsorption of  $\gamma$ -APS onto aluminum mirrors from 1% aqueous solutions at the natural pH (10.4), the structure of the films depended on the adsorption time. Films formed during one minute adsorption were characterized by absorption bands near 2920, 1630, 1570, 1470, 1330, and 1100  $\text{cm}^{-1}$  (see Figure 16B). This spectrum is very similar to spectra obtained from  $\gamma$ -APS adsorbed onto iron at comparable pH values (see Figure 5A). Observation of the infrared bands near 1570 and 1470  $\text{cm}^{-1}$  probably indicates the formation of an amine bi-

carbonate for  $\gamma$ -APS adsorbed onto aluminum at pH 10.4. Observation of the SiO asymmetric stretching mode near  $1100\text{ cm}^{-1}$  indicates formation of a siloxane polymer.

Films formed during fifteen minutes adsorption at pH 10.4 were characterized by a strong absorption band near  $1080\text{ cm}^{-1}$ , a weak, broad band extending from about  $1650\text{ cm}^{-1}$  to about  $1500\text{ cm}^{-1}$ , and a weak band near  $2920\text{ cm}^{-1}$  (see Figure 16C). The strong band near  $1080\text{ cm}^{-1}$  indicates polysiloxane formation but the low frequency of this band compared to that observed for similar films on iron may indicate substantial interaction between  $\gamma$ -APS and the oxidized surface of the aluminum mirrors. In fact, when the reflection accessory was removed from the reference beam of the spectrophotometer enabling the oxide absorption band for the sample mirrors to be studied, it was observed that the absorption band near  $960\text{ cm}^{-1}$ , which is characteristic of the air formed oxide, decreased in intensity during adsorption of  $\gamma$ -APS at pH 10.4 for fifteen minutes, indicating dissolution of the oxide and, perhaps, deposition of an aluminum/ $\gamma$ -APS complex on the surface. The broad, weak band extending from  $1650$  to  $1500\text{ cm}^{-1}$  may be related to hydrogen bonding of the amino groups or, perhaps, to formation of a complex with metal ions.

Results obtained from X-ray photoelectron spectroscopy were consistent with those obtained from infrared spectroscopy. However, in some cases the XPS spectra provided new information regarding the interaction between  $\gamma$ -APS and the oxidized surface of aluminum. The XPS spectrum of  $\gamma$ -APS adsorbed onto aluminum at pH 8.5 is shown in Figure 17A and several interesting features may be noted. The nitrogen 1s binding energy is near 402.0 eV. This value is somewhat above that usually observed for free primary amino groups ( $\sim 399.5$  eV), indicating that the amino groups in  $\gamma$ -APS adsorbed at pH 8.5 are protonated, probably as hydrochlorides. The oxygen 1s binding energy is observed near 532.6 eV, a value charac-

teristic of siloxane polymers. The aluminum 2p band near 75.7 ev is substantially stronger than the silicon 2p band near 102.9 ev, indicating that the  $\gamma$ -APS films were quite thin or, perhaps, that aluminum was included in the films. The strong aluminum signal could also indicate a discontinuous film. As indicated above, Auger images from  $\gamma$ -APS films adsorbed onto iron indicated that continuous films were obtained in that case. However, similar Auger investigations are needed to determine whether the  $\gamma$ -APS films adsorbed onto aluminum are also continuous.

The XPS spectrum of  $\gamma$ -APS adsorbed onto aluminum from 1% aqueous solutions at pH 10.4 for one minute is shown in Figure 17B. In this case the nitrogen 1s binding energy is observed near 400.8 ev. This value is intermediate between those usually observed for free and protonated amino groups and may indicate formation of an amine complex. However, more work is needed to verify such an assignment. The aluminum and silicon bands near 75.7 and 102.9 ev, respectively, are more nearly equal in intensity than for films formed at pH 8.5, probably indicating that the  $\gamma$ -APS films formed at pH 10.4 were somewhat thicker than those obtained at pH 8.5. It is interesting to note that a weak band characteristic of copper was observed near 933.5 ev for  $\gamma$ -APS adsorbed onto aluminum at pH 10.4 for one minute. Copper is, of course, the major alloying element in 2024 aluminum and there may be some tendency for copper to segregate near the surface or even to complex with  $\gamma$ -APS during treatment of the aluminum mirror with an aqueous solution of  $\gamma$ -APS at pH 10.4. Similar segregation of copper near the surface during FPL etching of 2024 aluminum has been reported (18).

The XPS spectrum of  $\gamma$ -APS adsorbed onto aluminum from 1% aqueous solutions at pH 10.4 for 15 minutes is shown in Figure 17C. The nitrogen 1s binding energy was again observed near 400.8 ev, indicating possible formation of a complex with metal ions. However, the most inter-

esting aspect of Figure 17C concerns the large band characteristic of copper that is observed near 933.5 eV. This result implies a substantial accumulation of copper near the surface during extended treatment of 2024 alloy with aqueous solutions of  $\gamma$ -APS at pH 10.4 and could be especially significant considering that large concentrations of copper at the interface may be related to poor hydrothermal stability of adhesive bonds to aluminum (18).

We have also determined the structure of films formed by the adsorption of  $\gamma$ -GPS onto aluminum from aqueous solutions. However, as indicated above, only poorly reproducible, discontinuous films were formed on aluminum mirrors unless a few drops of acetic acid were added to the solution to catalyze hydrolysis of the silane. The spectrum shown in Figure 18 was typical of those obtained from mirrors immersed in such catalyzed solutions and then withdrawn at a rate of 0.125 in/min. A single strong band was observed near  $1105\text{ cm}^{-1}$  while a weaker band was observed near  $1190\text{ cm}^{-1}$ . The transmission infrared spectrum of  $\gamma$ -GPS is dominated by bands near 1200, 1085, and  $820\text{ cm}^{-1}$  (see Figure 9A) that are associated with the  $\text{SiOCH}_3$  groups. The virtual absence of the bands near 820 and  $1085\text{ cm}^{-1}$  from the spectrum in Figure 18, along with the reduced intensity of the band near  $1190\text{ cm}^{-1}$ , indicates that the films formed on aluminum are highly hydrolyzed. However, the strong band near  $1105\text{ cm}^{-1}$  is characteristic of siloxane polymers, indicating polymerization of the silanols resulting from such hydrolysis. The spectra of  $\gamma$ -GPS films on aluminum were always similar to those formed on iron (see Figure 9B), indicating that the interaction with the oxidized surfaces of iron and aluminum most likely involves hydrogen bonding. However, the nature of the interaction between  $\gamma$ -GPS and these substrates is still under investigation.

We have also prepared single lap shear adhesive joints in order to determine the effectiveness of  $\gamma$ -APS and  $\gamma$ -GPS as primers for improving

the wet strength of aluminum/epoxy adhesive joints. The results are shown in Figure 19. The strength of unprimed joints dropped quickly during the first ten days of water immersion and then stayed rather constant to times as long as 40 days. This result was attributed to corrosion of the substrate and a change in the locus of failure from cohesive within the epoxy to cohesive within the oxide. Results obtained from scanning electron microscopy supported this conclusion. As shown in Figure 20A, dry unprimed joints clearly failed within the epoxy. However, severe corrosion was typically observed on fracture surfaces of unprimed joints that had been immersed for up to 40 days (see Figure 20B).  $\gamma$ -GPS was an effective primer for aluminum for times as long as 20 days but the strength of joints primed with  $\gamma$ -GPS seemed to decrease somewhat after 40 days. Results obtained from SEM indicated that the  $\gamma$ -GPS primer greatly inhibited the corrosion of the substrate. Dry primed joints obviously failed cohesively within the adhesive as expected. However, the fracture surfaces of primed joints immersed for up to 40 days also showed some evidence of failure within the epoxy and little evidence of corrosion. Patrick obtained somewhat similar results for  $\gamma$ -APS primers on aluminum tapered double cantilever beams bonded with an amine-cured epoxy (2). Considerable corrosion was observed on the fracture surfaces of joints prepared from unprimed adherends but little corrosion was observed on the fracture surfaces of joints prepared from adherends primed with  $\gamma$ -APS (2).

Reference to Figure 19 indicates that  $\gamma$ -APS was always a more effective primer for aluminum than was  $\gamma$ -GPS. Moreover, the breaking strength of joints prepared from adherends primed with  $\gamma$ -APS was rather constant after about 10 days immersion at 60°C and did not decrease significantly even after 40 days immersion. This result was somewhat different from those obtained for  $\gamma$ -APS on iron. In that case there was a fast initial decrease in breaking strength followed by a slower, more gradual decrease. The reasons for this are still under investigation using SEM, XPS, and

AES to determine the locus of failure. However, it seems as though  $\gamma$ -APS inhibits the corrosion of the substrate leading to failure that is near the interface but within the adhesive after 40 days. It is also interesting to note that the pH of the  $\gamma$ -APS primer solution is relatively unimportant for aluminum adherends. This result is also considerably different from those previously obtained for iron and may be related to the rather low molecular weight of the polysiloxanes formed by  $\gamma$ -APS adsorbed onto aluminum. Analysis of the fracture surfaces as indicated above is expected to clarify this point.

### C. Titanium substrates

The surface of freshly polished titanium-6Al, 4V mirrors was characterized using AES (see Figure 21). Titanium, carbon, and oxygen were the only elements detected in significant concentrations. As usual, the carbon was easily removed by a few minutes sputtering, indicating that the carbon was probably related to adsorbed hydrocarbons. Small amounts of zinc and silicon were also detected but easily removed by sputtering.

Films of  $\gamma$ -APS were formed on freshly polished titanium mirrors by immersing the mirrors in 1% aqueous solutions for appropriate times, withdrawing the mirrors, and blowing the excess solution off the mirrors using a strong stream of nitrogen. Results obtained from ellipsometry indicated that the films obtained were typically about 100 Å in thickness. The infrared spectra obtained from such films were similar to spectra of  $\gamma$ -APS adsorbed onto iron. Films formed at pH 10.4 were characterized by infrared bands near 1570, 1470, and 1070  $\text{cm}^{-1}$  (see Figure 22A). As indicated above, the bands near 1570 and 1470  $\text{cm}^{-1}$  are probably related to a bicarbonate. The band near 1070  $\text{cm}^{-1}$  is characteristic of a low molecular weight siloxane polymer. Films formed by adsorption of  $\gamma$ -APS onto titanium mirrors at pH 10.4 were unstable during exposure to the laboratory atmosphere. After 5 hours of such exposure, the spectrum shown in Figure 22B was obtained from the mirrors used to obtain the spectrum in Figure

22A. After three days the spectrum shown in Figure 22C was obtained. The band near  $1070\text{ cm}^{-1}$  split into components near  $1140$  and  $1040\text{ cm}^{-1}$ , indicating additional polymerization to form a high molecular weight polysiloxane. Some tendency for the band near  $1470\text{ cm}^{-1}$  to decrease in intensity and for the band near  $1570\text{ cm}^{-1}$  to increase in frequency during atmospheric exposure was also observed.

Very similar results have been obtained during atmospheric exposure of  $\gamma$ -APS films adsorbed onto iron at pH 10.4 (7). However,  $\gamma$ -APS films adsorbed onto aluminum at pH 10.4 were stable during such exposure (19). These results indicate that there is a significant difference in the interaction between  $\gamma$ -APS and the oxidized surfaces of iron and titanium and between  $\gamma$ -APS and the oxidized surface of aluminum. In the former case, such interaction is probably mostly through hydrogen bonding. In the latter case the interaction may involve the formation of complexes through the amino groups and, perhaps, the formation of some SiOAl bonds, possibly through formation of polymers on the surface.

Some results have already been obtained concerning the use of  $\gamma$ -APS as a primer for improving the wet strength of epoxy/titanium lap joints immersed in water at  $60^\circ\text{C}$  and are summarized in Table I below.

Table I  
Breaking Strength of Titanium/Epoxy Lap Joints  
Immersed in Water at  $60^\circ\text{C}$

Immersion Time (days)	Average Shear Stress (psi)		
	no primer (control)	primed with $\gamma$ -APS at pH 10.4	primed with $\gamma$ -APS at pH 8.0
10		1943	1885
20	871	1755	1961
40	959	1732	1759

These results indicate that  $\gamma$ -APS is extremely effective as a primer for improving the hydrothermal stability of epoxy/titanium adhesive joints. After 40 days in water at 60°C, joints prepared from adherends pretreated with  $\gamma$ -APS prior to adhesive bonding were nearly twice as strong as joints prepared from unprimed adherends.

These results are quite similar to those previously obtained for iron where  $\gamma$ -APS was also found to be an extremely effective primer. However, it is interesting to note that lowering the pH of the silane solution from 10.4 to 8.0 resulted in even better performance of the  $\gamma$ -APS primer on iron but not titanium. This effect is still under investigation but may be related to orientation of  $\gamma$ -APS on the surface (18). The isoelectric point of the oxide on iron is near pH 9.0. Therefore, at pH 10.4  $\gamma$ -APS may adsorb onto the surface of iron "upside down" with the amino group adjacent to the oxide (20). However, at pH 8.0  $\gamma$ -APS would adsorb through the silanol groups as suggested by the chemical bonding theory (see Figure 1). The isoelectric point of the oxide on titanium is near 6.0 and  $\gamma$ -APS may adsorb on titanium "upside down" at both pH 10.4 and 8.0. The performance of  $\gamma$ -APS primers may be even better at pH values nearer to 6.0. This possibility is presently being investigated.



## V. Conclusions

The results obtained here indicate that the silanes investigated,  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS) and  $\gamma$ -glycidoxypropyltrimethoxysilane ( $\gamma$ -GPS), are both effective as primers for improving the wet strength of metal-to-metal adhesive joints using aluminum, titanium and iron adherends and epoxy adhesives. However, the results obtained so far also indicate that the silanes are most effective on metals such as titanium and iron that have relatively stable oxides.  $\gamma$ -APS and  $\gamma$ -GPS form well polymerized polysiloxanes that interact with such substrates by hydrogen bonding.  $\gamma$ -APS is quite reactive toward the oxidized surface of aluminum and forms less polymerized polysiloxanes on such a surface. This may indicate that a modification of the "chemical bonding" theory will in fact explain the mechanism by which silanes function.

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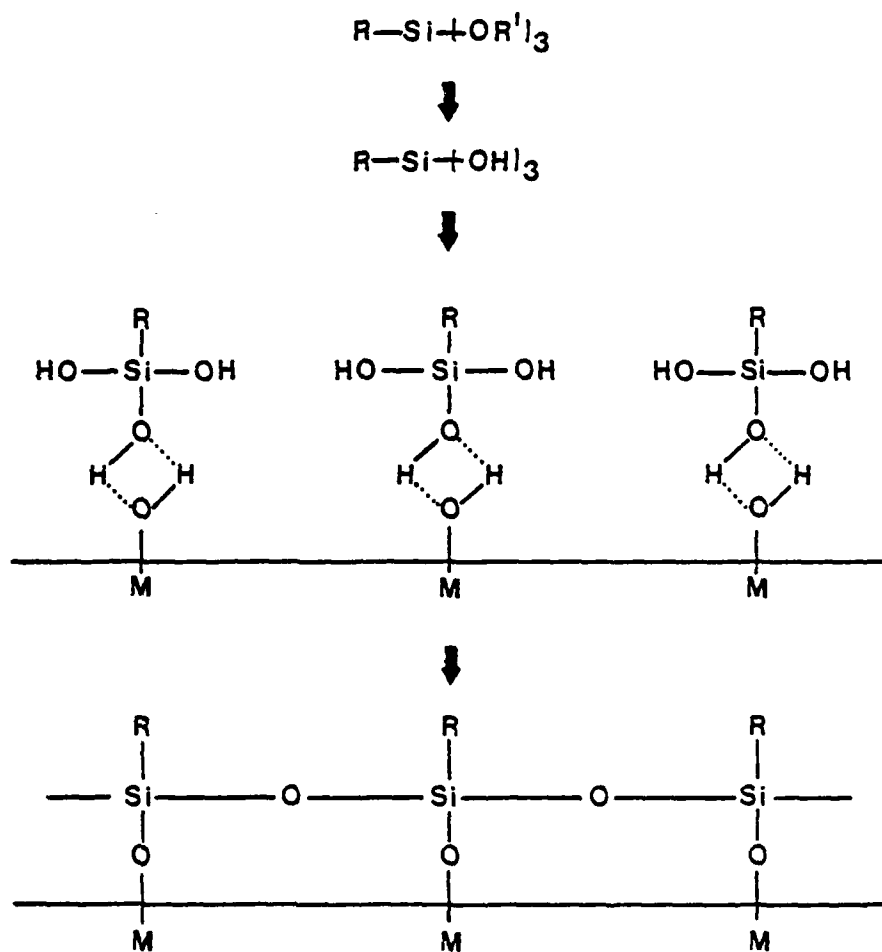


Figure 1. The chemical bonding model for explaining the role of organosilanes as primers for improving the wet strength of adhesive joints.

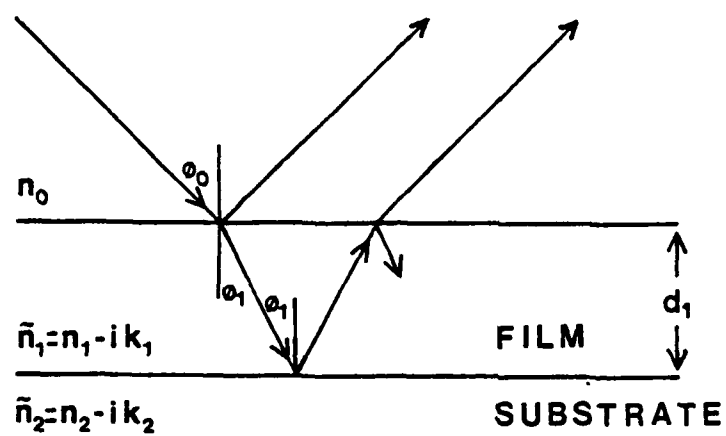


Figure 2. Model for treating reflection from film - covered metal as a boundary value problem.

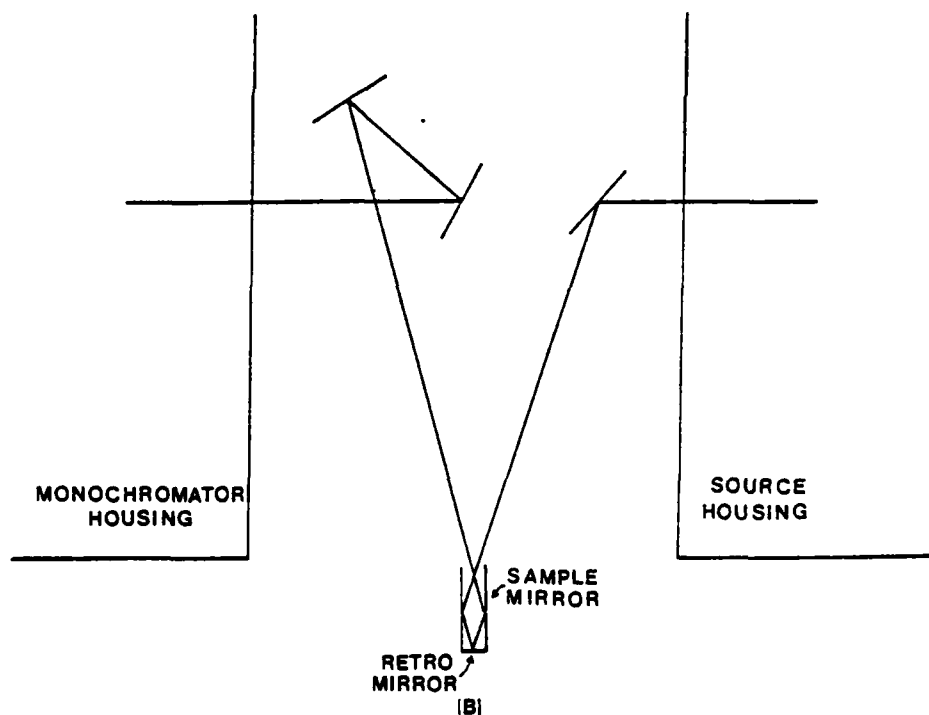
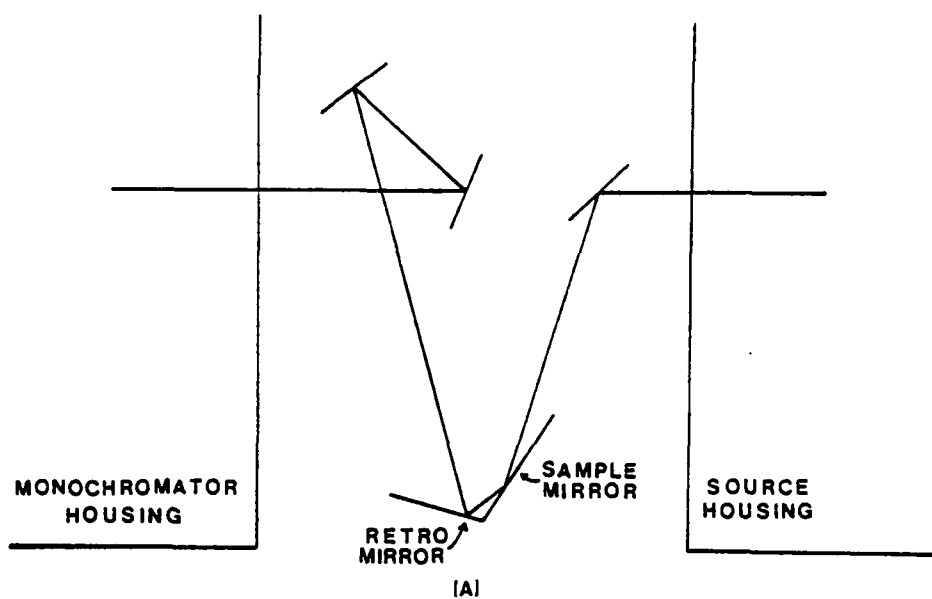


Figure 3. Sampling arrangement for external reflection infrared spectroscopy using (A) - 1 reflection at any angle of incidence and (B) - any number of reflections at  $78^\circ$  angle of incidence.

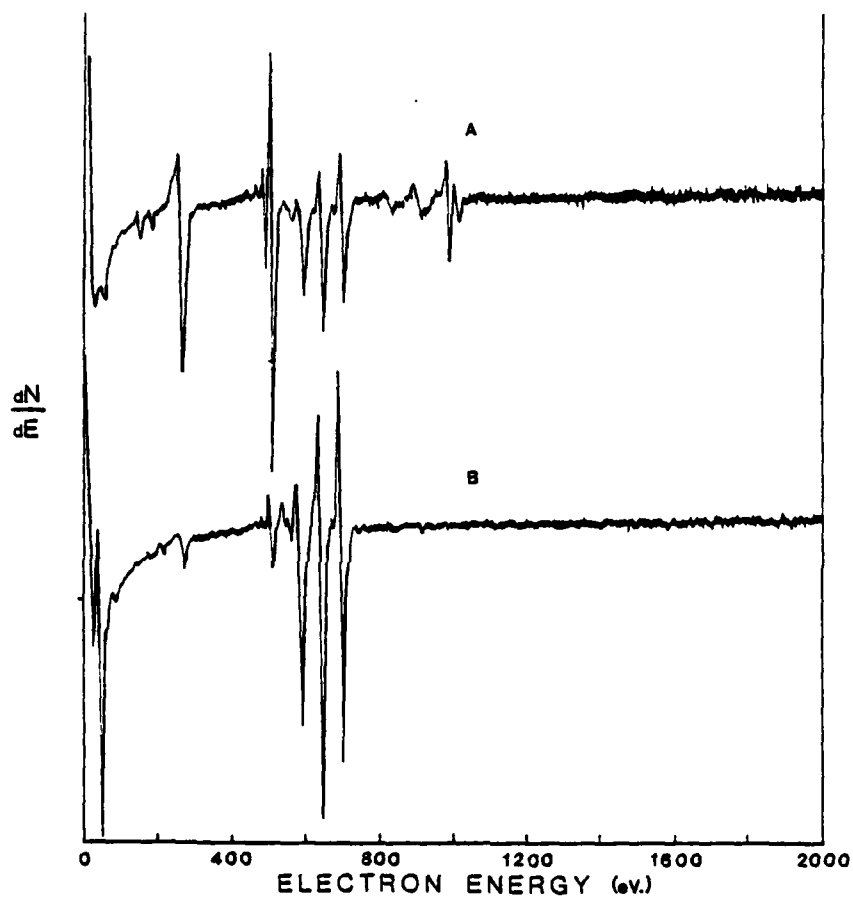


Figure 4. Auger electron spectrum of iron mirrors (A) - immediately after mechanical polishing and (B) - after ten minutes sputtering.

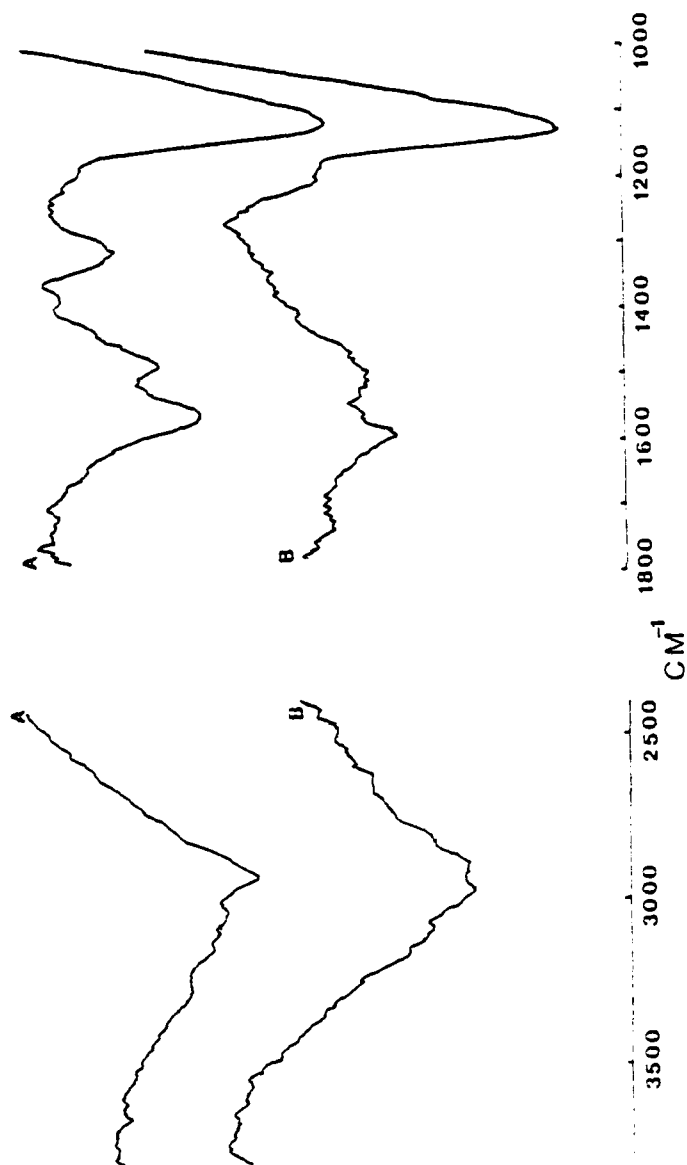


Figure 5. Reflection-absorption infrared spectra of  $\gamma$ -APS films adsorbed onto iron mirrors from 1% aqueous solutions at (A) pH 10.4 and (B) pH 8.0.



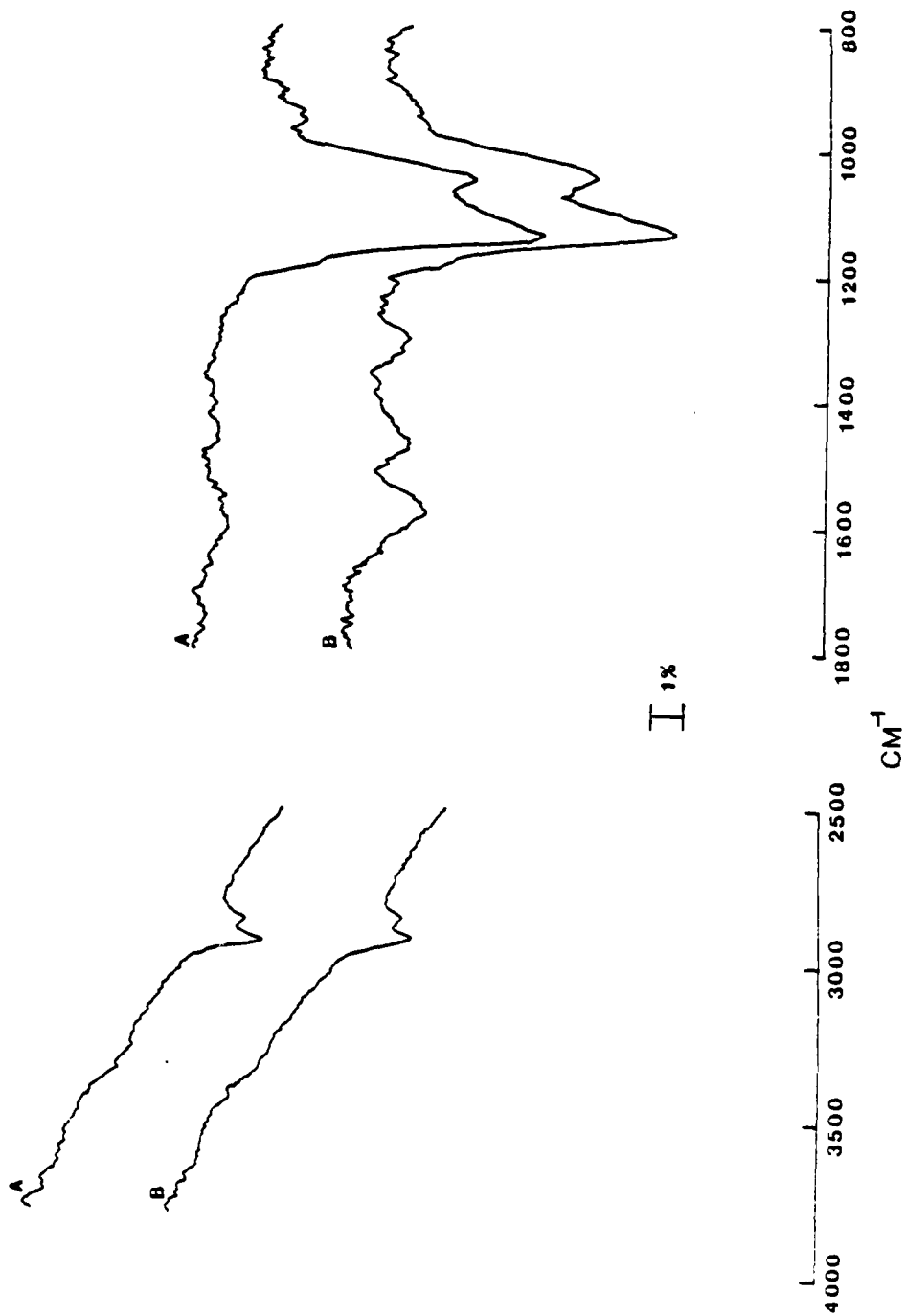


Figure 6. Infrared spectra of  $\gamma$ -APS adsorbed onto iron from 1% aqueous solutions at pH 10.4 and (A) maintained in nitrogen atmosphere and (B) maintained in dried air.

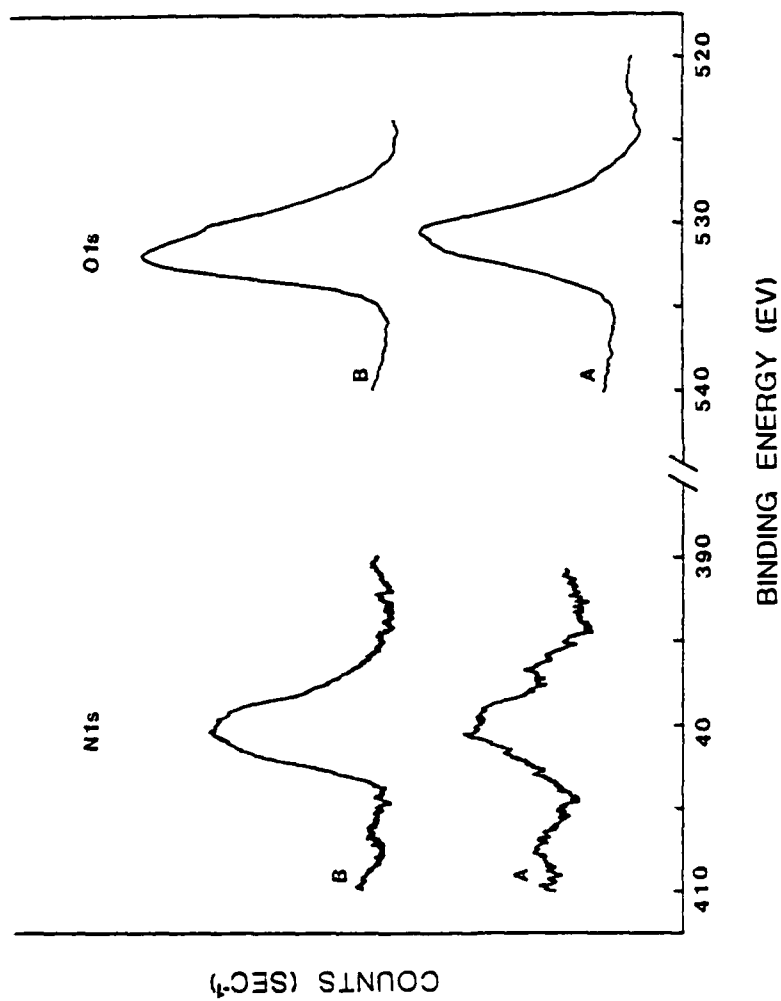


Figure 7. X-ray photoelectron spectra of  $\gamma$ -APS adsorbed onto iron from (A) - 0.4% and (B) - 1% aqueous solutions at pH 8.0.

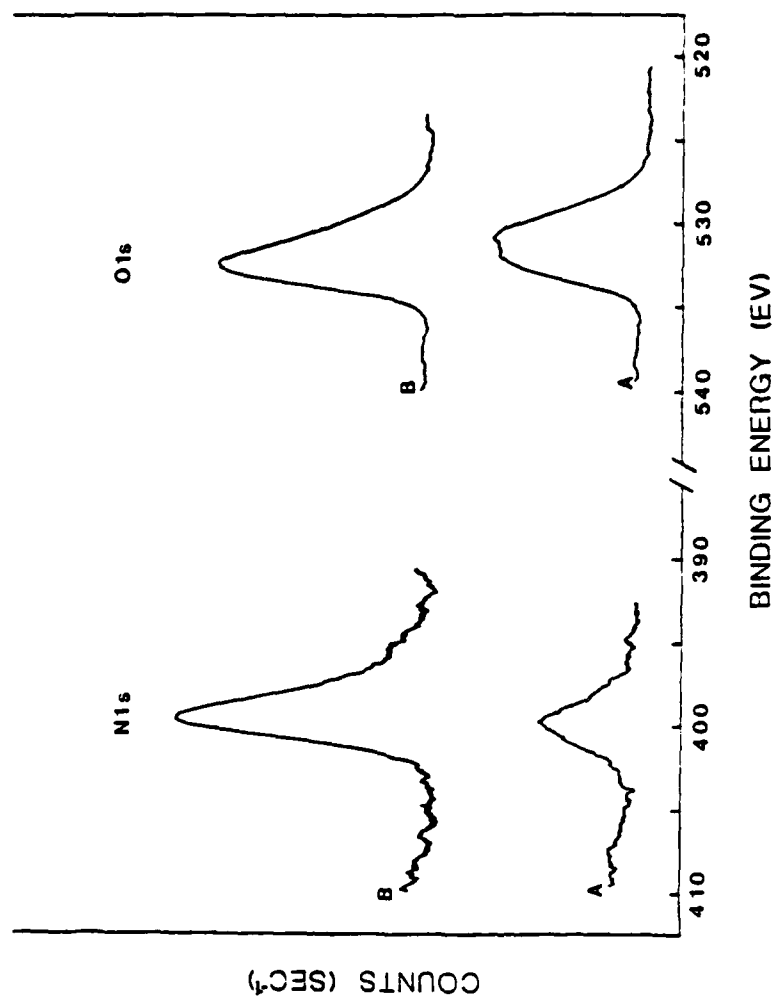


Figure 8. X-ray photoelectron spectra of  $\gamma$ -APS adsorbed onto iron from (A) - 0.4% and (B) - 1% aqueous solutions at pH 10.4.

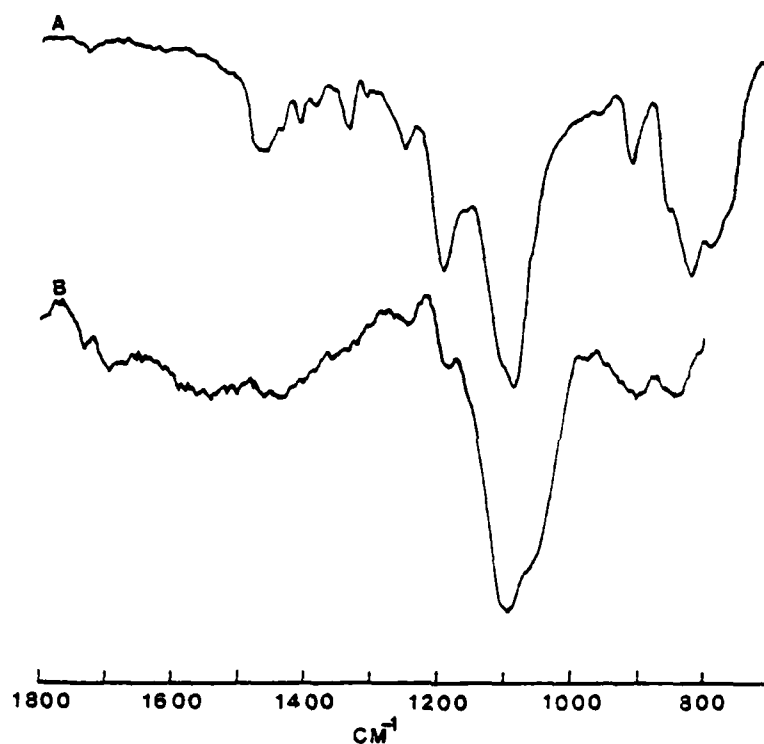


Figure 9. Infrared spectra of (A)  $\gamma$ -glycidoxypropyltrimethoxysilane monomer and (B) film formed by adsorption of  $\gamma$ -GPS onto iron mirrors from 1% aqueous solution at pH 4.0.

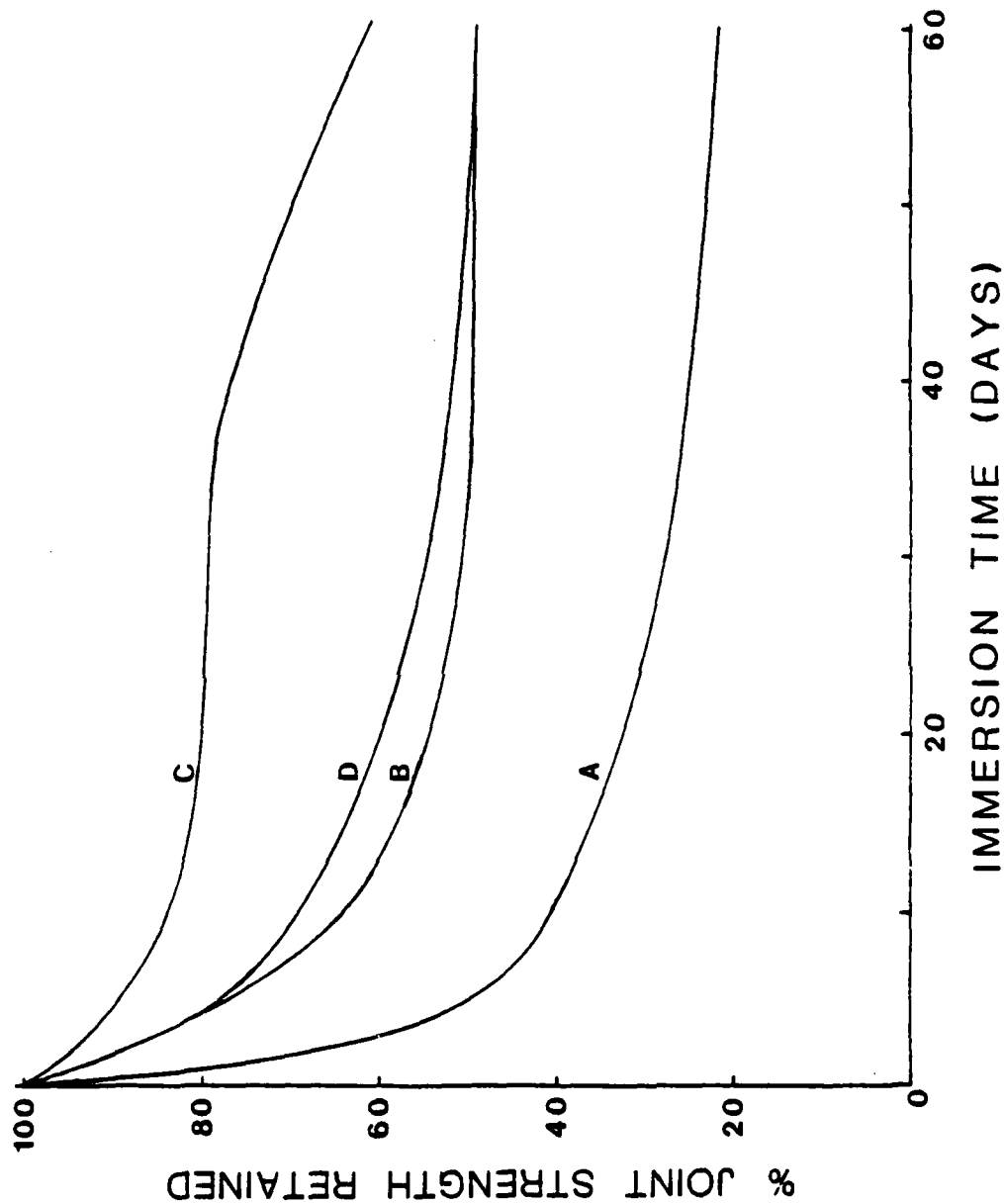


Figure 10. Breaking strength versus immersion time in water at 60°C for iron/epoxy lap joints prepared with (A) - no primer, (B) - 1%  $\gamma$ -APS at pH 10.4, (C) - 1%  $\gamma$ -APS at pH 8.0, and (D) - 1%  $\gamma$ -GPS at pH 4.0.

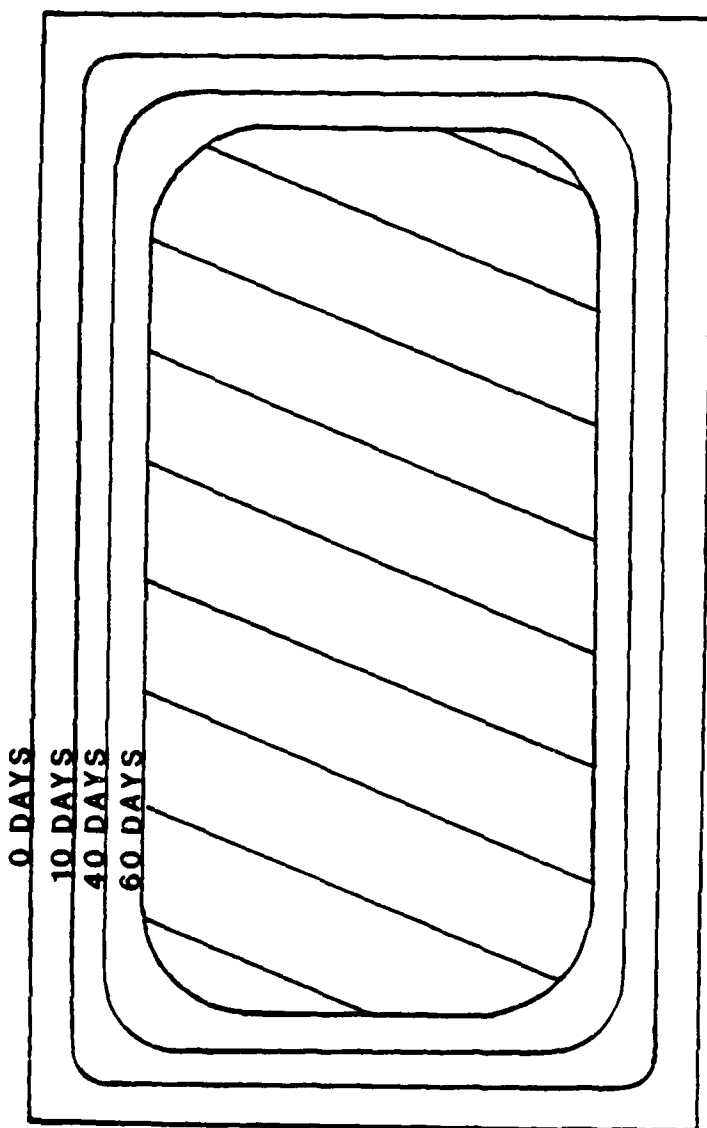


Figure 11. Contours showing critical concentration of water (1.37 grams of water per 100 grams of adhesive) in lap joints at 60°C as a function of time.

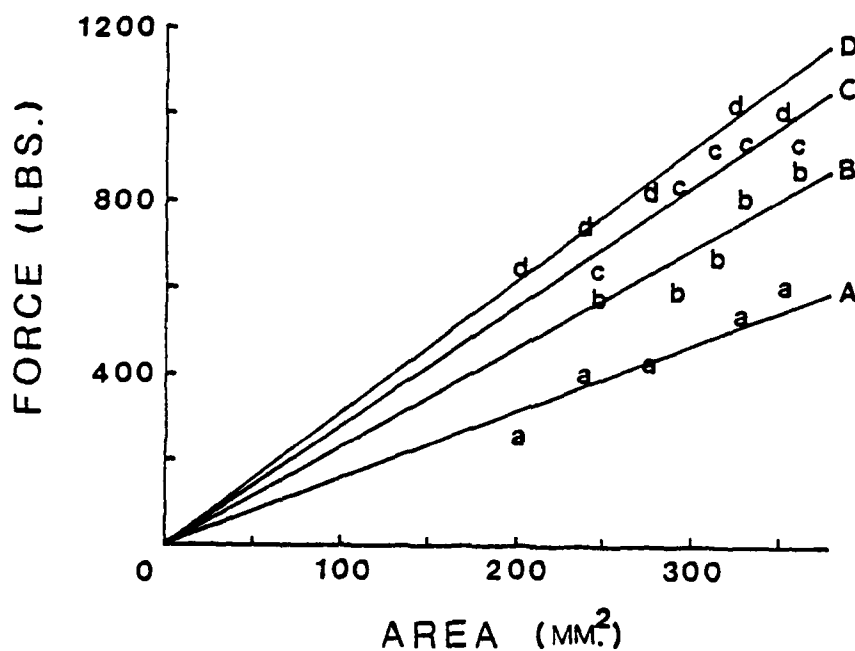


Figure 12. Breaking force versus bonded area for iron/epoxy lap joints immersed in water at 60°C: (A) - no silane primer, (B) - 1%  $\gamma$ -APS at pH = 10.4, (C) - 1%  $\gamma$ -APS at pH = 8.0, and (D) - 1%  $\gamma$ -GPS at pH = 4.0. Critical concentration equals 1.37 gm water/100 gm adhesive in (A) and (D) and 1.56 gm water/100 gm adhesive in (B) and (C).

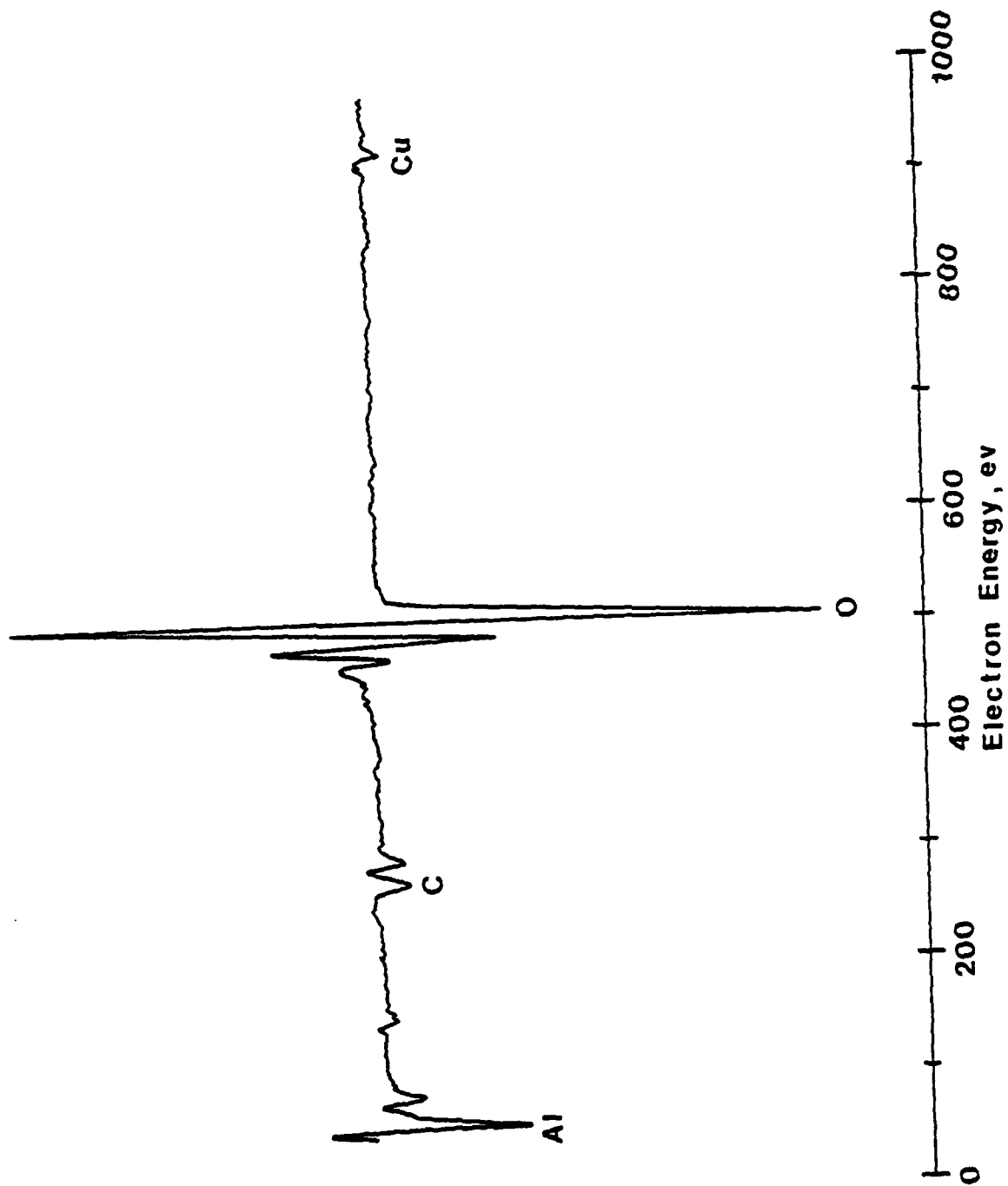


Figure 13. Auger electron spectrum of mechanically polished 2024 aluminum alloy.



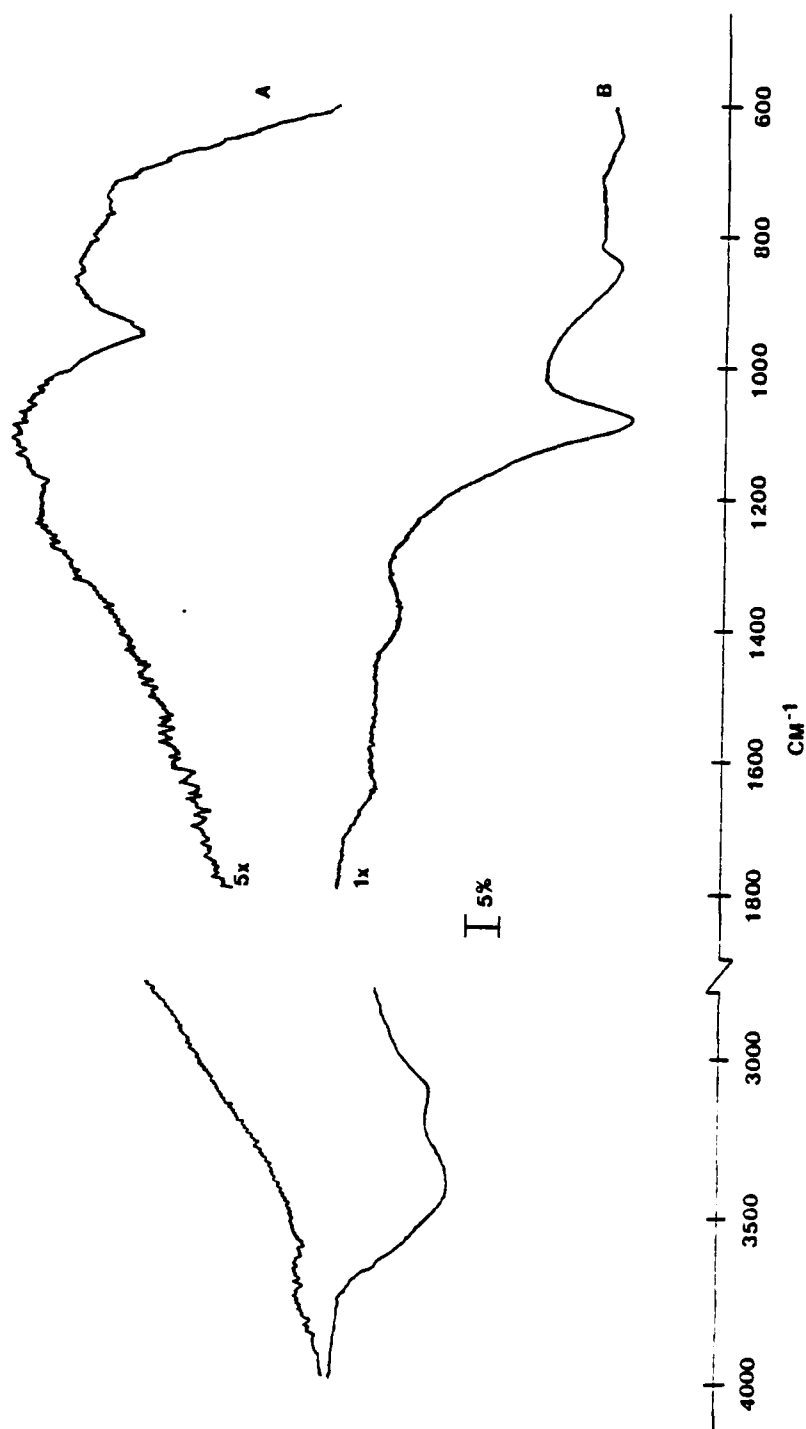


Figure 14. Infrared spectra of oxides formed on mechanically polished 2024 aluminum alloy: (A) - natural oxide; (B) - oxide obtained after immersion in boiling water for five minutes.

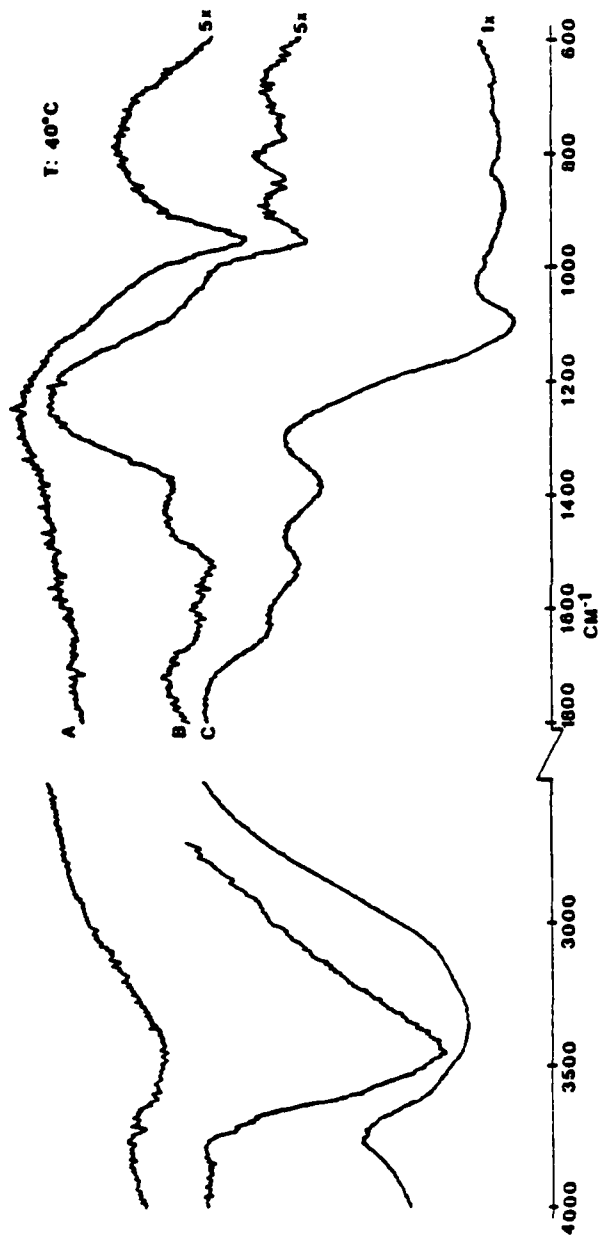


Figure 15. Infrared spectra oxides formed on mechanically polished 2024 aluminum alloy during immersion in water at 40°C for (A) - one hour, (B) - 16 hours, and (C) - 24 hours.

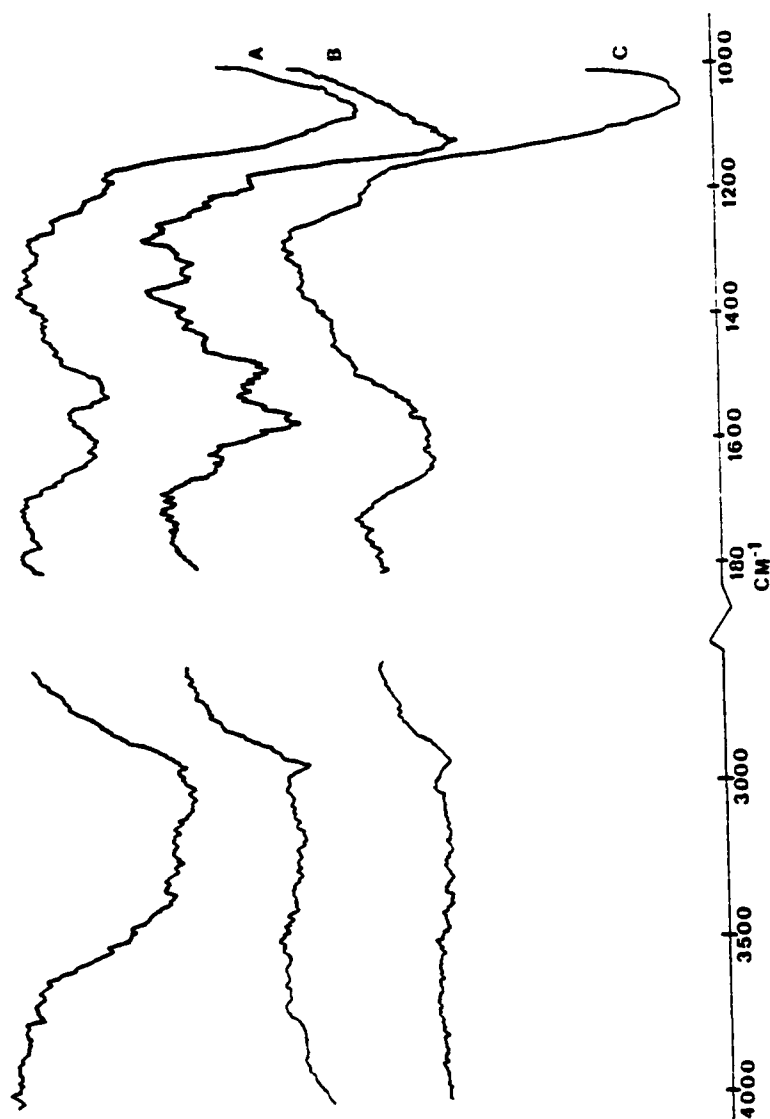


Figure 16. Infrared spectra of films formed by adsorption of  $\gamma$ -APS onto aluminum mirrors:  
(A) - 15 minutes adsorption at pH 8.5; (B) - 1 minute adsorption at pH 10.4;  
(C) - 15 minutes adsorption at pH 10.4.

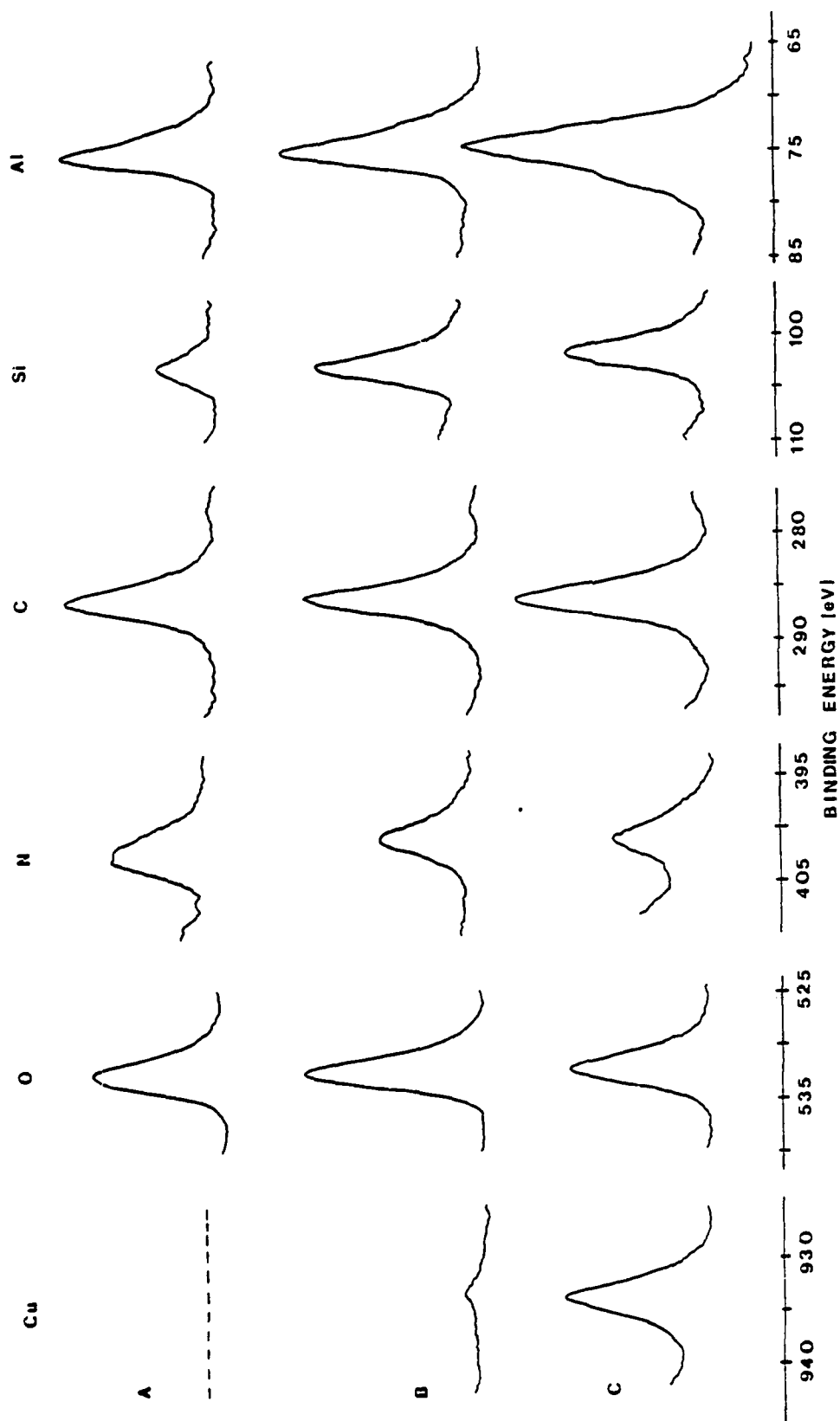


Figure 17. X-ray photoelectron spectra of films formed by adsorption of  $\gamma$ -APS onto aluminum mirrors: (A) - 15 minutes adsorption at pH 8.5; (B) - 1 minute adsorption at pH 10.4; (C) - 15 minutes adsorption at pH 10.4.

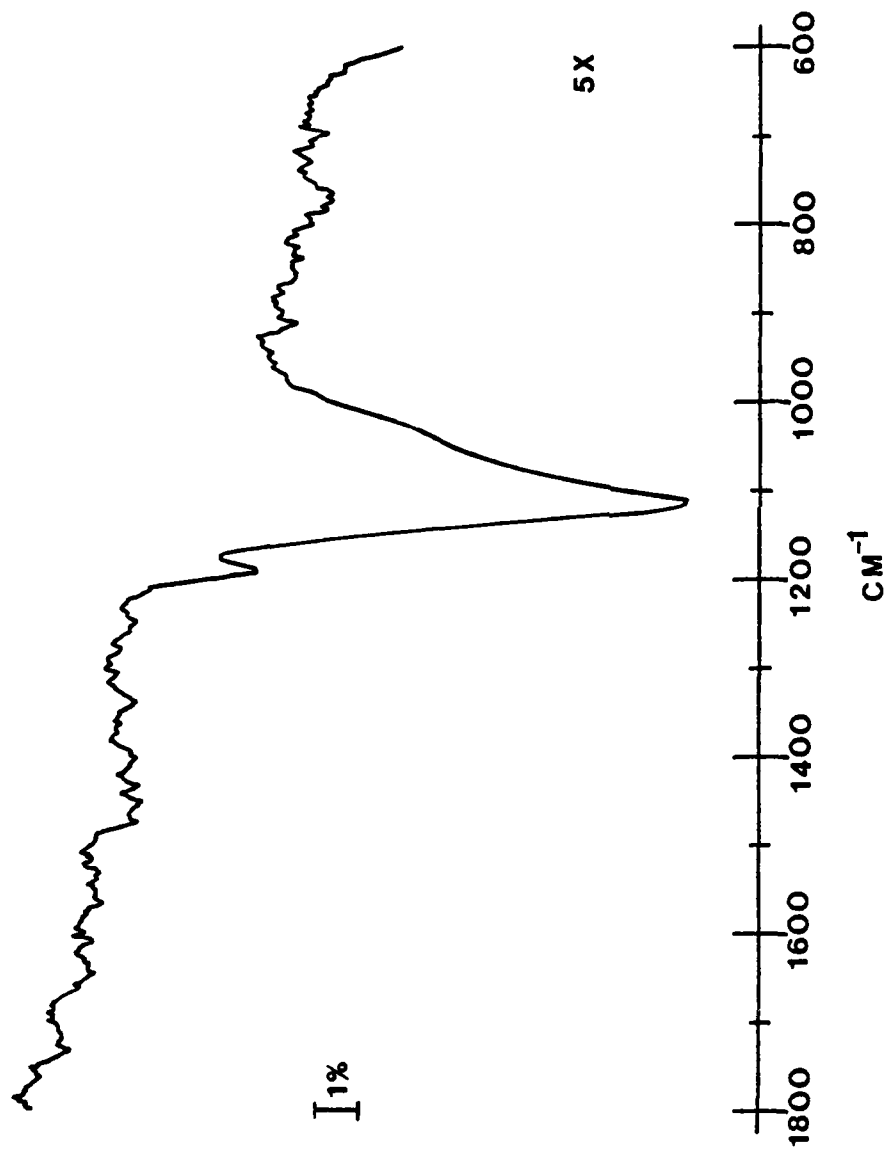


Figure 18. Infrared spectrum of  $\gamma$ -glycidypropyltrimethoxysilane adsorbed onto aluminum from catalyzed 1% aqueous solution.

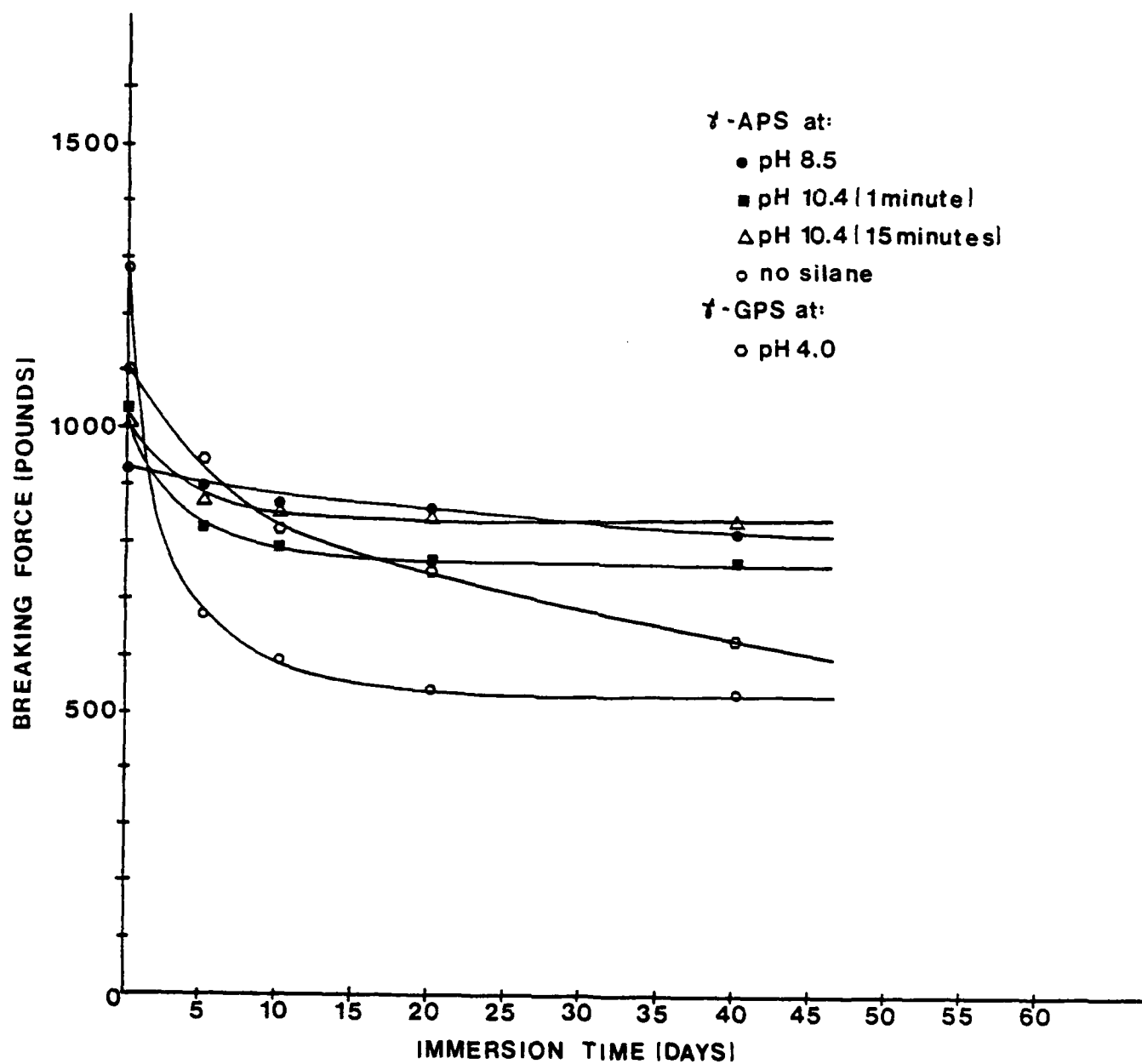
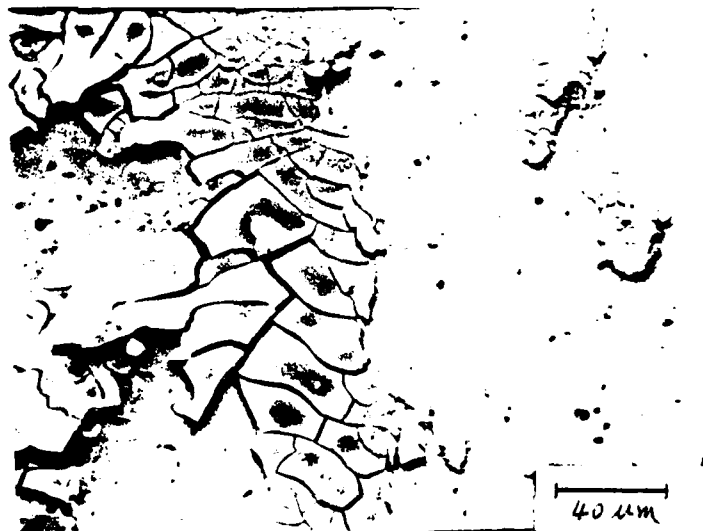


Figure 19. Breaking strength of aluminum/epoxy lap joints immersed in water at 60°C.



(a)



(b)

Figure 20. Scanning electron micrographs obtained from fracture surfaces of unprimed aluminum/epoxy lap joints prepared from unprimed adherends and fractured (A) dry and (B) after 40 days immersion in water at 40°C.

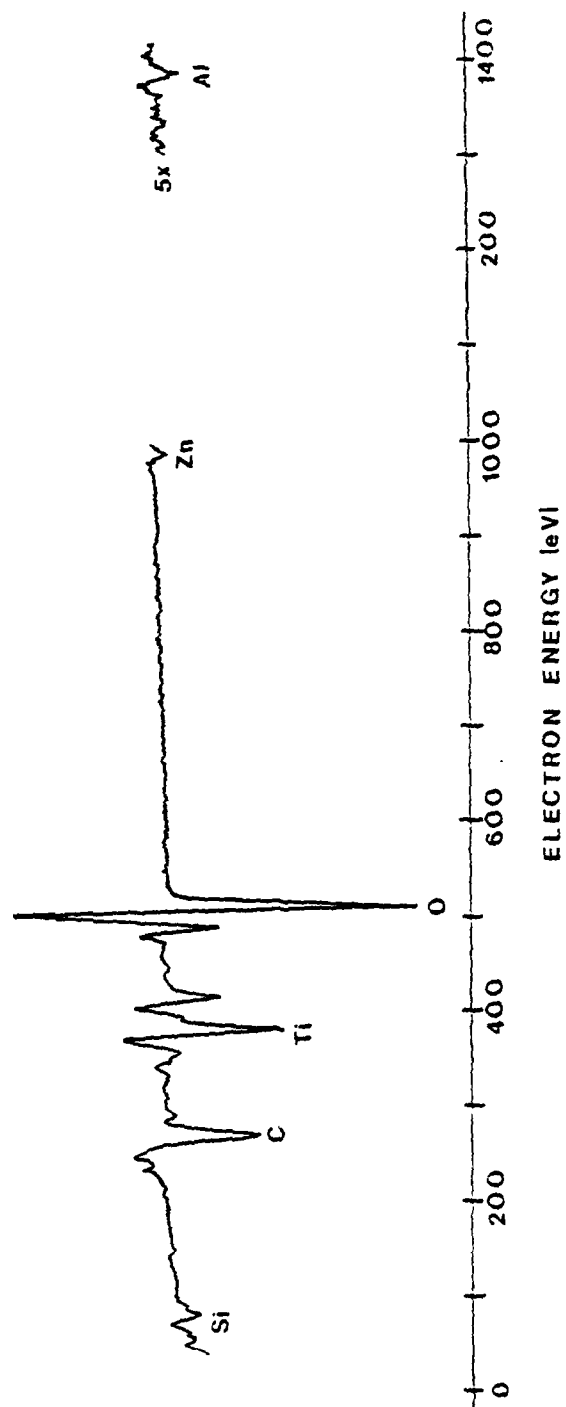


Figure 21. Auger electron spectrum of freshly polished titanium-6Al, 4V mirrors.



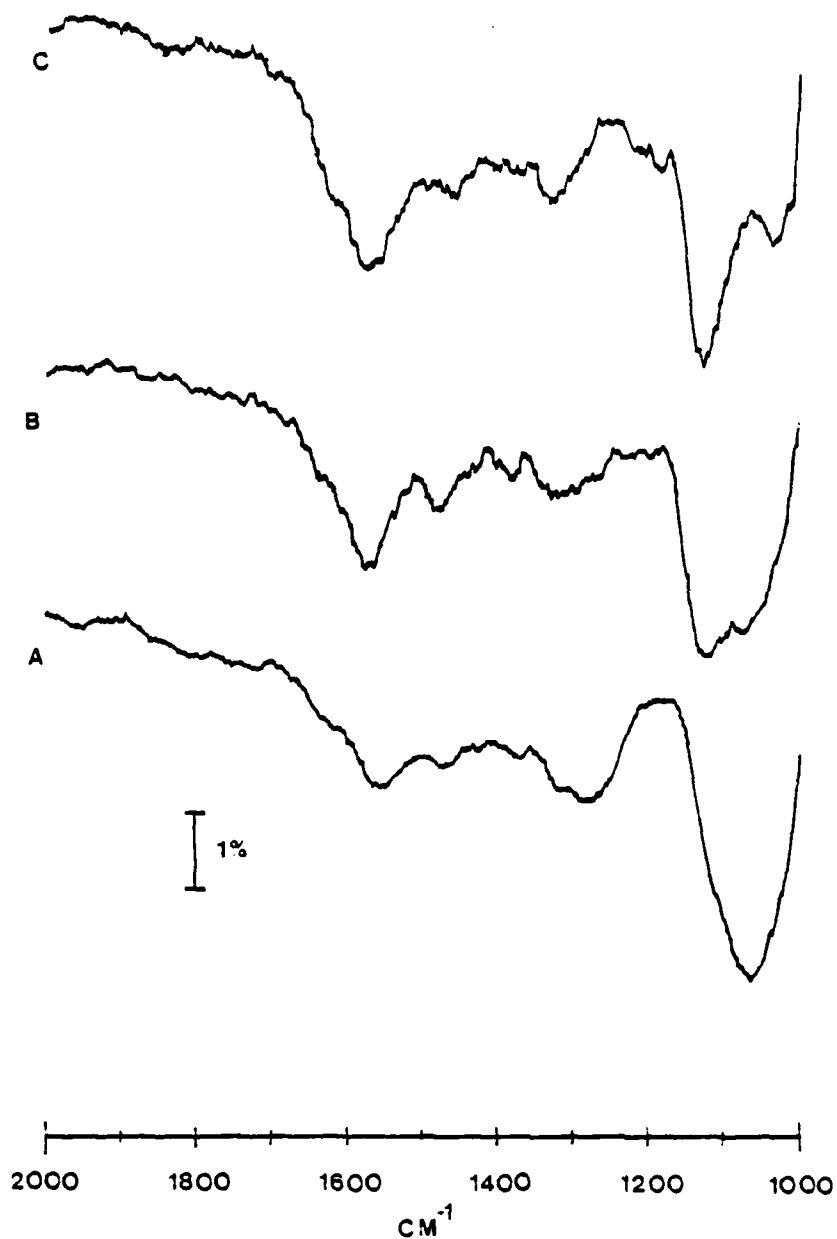


Figure 22. Infrared spectra of films formed by  $\gamma$ -APS adsorbed onto titanium mirrors from 1% aqueous solutions at pH 10.4: (A) - immediately after adsorption; (B) - after exposure to laboratory atmosphere for 5 hours; (C) - after exposure to laboratory atmosphere for 3 days.

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